〔54〕发明名称 源于丙交酯的可降解热塑性塑料

〔57〕摘要

本发明是关于丙交酯及其混合物的增塑聚合物，可用它们制成环境生物降解的制品，这种制品具有常规塑料的特征并可代替它们。另外还涉及一种可作为结晶聚苯乙烯替代物的材料及其制备方法。第三方面涉及将常规热塑性塑料与聚乳酸共混，制备出新型的包装材料。本发明的第四方面是关于将可相容的弹性体与聚丙交酯共混，得到耐冲击的改性聚丙交酯。

<21>

（BJ）第1456号

1. 一种可在环境中生物降解的组合物，它可以作为热塑性聚合物组合物的替代物，上述组合物包括经增塑剂增塑的具有下式的聚合物

$$\left(\!\!-\begin{array}{c}CH_3\\|\\C\\|\\H\end{array}\!-\begin{array}{c}O\\\|\\C\end{array}\!-O\!-\right)\!n$$
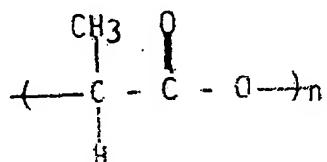
式中 n 是整数，代表重复单元的数目，且 $150 < n < 20000$，该未取向组合物的拉伸强度为300-20000psi，断裂伸长率为50-1000%，正切模量为2000-250000psi，所述增塑剂选自丙交酯、乳酸低聚物、丙交酯低聚物及它们的混合。

2. 按权利要求1的组合物，其中聚合物是由选自L-丙交酯、D-丙交酯、内消旋D,L-丙交酯及其混合物的丙交酯单体制备的。

3. 按权利要求1的组合物，其中乳酸或丙交酯低聚物具有如下结构

$$\left(\!\!-\begin{array}{c}CH_3\\|\\C\\|\\H\end{array}\!-\begin{array}{c}O\\\|\\C\end{array}\!-O\!-\right)\!m$$
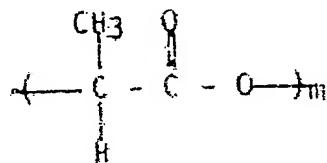
式中 m 是整数，且 $2 < m < 75$。

4. 按权利要求1的组合物，其中含有附加的增塑剂分散于该组合物中，所述增塑剂选自D-丙交酯、L-丙交酯、内消旋D,L-丙交酯、外消旋D,L-丙交酯和它们的混合物等单体，而且至少一部分上述分散的单体是与制备上述聚合物所用的单体立构相异的。

5．按权利要求1的组合物，其中含有低聚物分散在该组合物中，所述低聚物不是上述聚合物聚合期间生成的。

6．一种制备可在环境中生物降解的聚乳酸组合物的方法，包括：

a．制备丙交酯单体和催化剂，

b．将步骤(a)的单体聚合成为聚合物，反应温度要足够低，使反应在单体完全聚合之前停止，

c．监测步骤(b)中单体的量，以确定剩余单体的含量，

d．按步骤(c)测定的单体含量，在反应未完全之前停止步骤(b)的聚合，从而使预定量未反应的单体截留在聚合物中。

7．按权利要求6的方法，其中还包括：

e．将附加的增塑剂添加到该组合物中，所述增塑剂选自L-丙交酯、D-丙交酯、内消旋D,L-丙交酯、乳酸、丙交酯的低聚物、乳酸的低聚物和它们的混合物。

8．按权利要求7的方法，其中还包括选用与用来制备上述聚合物的单体立构相异的单体。

9．一种制备可生物降解的聚乳酸组合物的方法，包括：

a．制备丙交酯单体和催化剂，

b．将步骤(a)的单体溶液聚合成为聚合物，

c．向步骤(b)的聚合物添加增塑剂，所述增塑剂选自D-丙交酯、L-丙交酯、D,L-丙交酯、乳酸低聚物、丙交酯低聚物和它们的混合物。

10．使含有第一种可取向聚合物单元的热塑性聚合物组合物可以在环境中生物降解的方法，包括：

用未取向时拉伸强度为300-20000psi，断裂伸长率为50-1000%，正切模量为20000-250000psi 的第二种可取向聚合物代替第一种聚合物单元，所述第二种聚合物含有如下所示的聚乳酸单元：

$$\left(\begin{array}{c} CH_3 \\ | \\ C \\ | \\ H \end{array} - \begin{array}{c} O \\ || \\ C \end{array} - O\right)_n$$
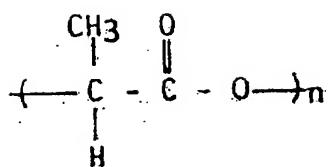
式中n 为整数，代表重复单元的数目，且 150＜n ＜20000，并且第二种聚合物是经增塑剂增塑的，所述增塑剂选自丙交酯、乳酸低聚物，丙交酯低聚物和它们的混合物。

11．使含有第一种可取向聚合物单元的聚烯烃组合物可以在环境中生物降解的方法，包括：

用未取向时拉伸强度为300-20000psi，断裂伸长率为50-1000%，正切模量为20000-250000psi 的第二种可取向聚合物代替第一种聚合物单元，所述第二种聚合物包括如下所示的聚乳酸单元：

$$\left(\begin{array}{c} CH_3 \\ | \\ C \\ | \\ H \end{array} - \begin{array}{c} O \\ || \\ C \end{array} - O\right)_n$$
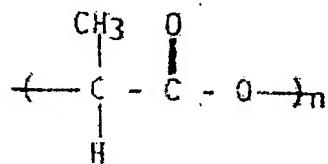
式中n 为整数，代表重复单元的数目，且 150＜n ＜20000，并且第二种聚合物是经增塑剂增塑的，所述增塑剂选自丙交酯、丙交酯低聚物、乳酸低聚物和它们的混合物。

12．一种可用作聚苯乙烯替代物的可在环境中生物降解的组合物，含有如下所示的聚乳酸单元：

$$\left(\begin{array}{c} CH_3 \\ | \\ C \\ | \\ H \end{array} - \begin{array}{c} O \\ || \\ C \end{array} - O\right)_n$$
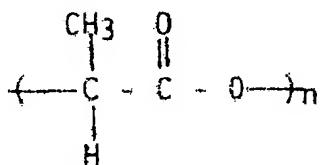
式中n 为介于75-10000的整数，α碳是L-构型和D-构型的混合物，其中D-构型单元偏多或L-构型单元偏多，所述第二种聚合物是由85-95%（重

4

量）L-丙交酯或D-丙交酯和15-5%（重量）D,L-丙交酯制备，其中分散有0.1-5%（重量）的增塑剂，第二种聚合物未取向时拉伸强度至少为5000psi，正切模量至少为200000psi。

13．按权利要求12的组合物，其中还含有分散在该组合物中的单体，所述单体选自D-丙交酯、L-丙交酯、内消旋D,L-丙交酯、外消旋D,L-丙交酯和它们的混合物，而且至少部分上述分散的单体是与用来制备上述聚合物的单体立构相异。

14．按权利要求12的组合物，其中还含有与在上述聚合物的聚合期间产生的低聚物立构相异的低聚物。

15．可用作聚苯乙烯替代物的可在环境中生物降解的组合物，含有下列组分的机械混合物：

a．具有下述聚乳酸单元的第一种聚合物：

$$\left[\begin{array}{c} CH_3 \\ | \\ -C - \\ | \\ H \end{array}\begin{array}{c} O \\ \| \\ C - O \end{array}\right]_n$$
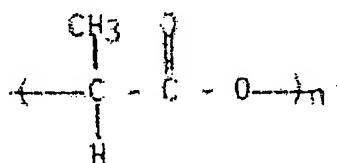
其中n 是介于75-10000的整数， $\alpha-$ 碳是L-构型和D-构型的混合物，其中D-构型单元偏多或L-构型单元偏多．

b．D-丙酯或L-丙交酯的均聚物，未取向组合物的拉伸强度至少为5000psi，正切模量至少为200000psi,其中还分散有增塑剂。

16．按权利要求15的组合物，其中含有0.1-5%（重量）分散的增塑剂。

17．按权利要求15的组合物，其中含有98-75%（重量）聚合的乳酸和2-25%（重量）丙交酯均聚物。

18．按权利要求15的组合物，其中含有选自D-丙交酯、L-丙交酯、内消旋D,L-丙交酯、乳酸、丙交酯低聚物．乳酸低聚物及其混合物的增

塑剂。

19. 按权利要求15的组合物，其中含有选自D-丙交酯、L-丙交酯、内消旋D,L-丙交酯、外消旋D,L-丙交酯及其混合物等单体的增塑剂，而且至少部分所述的分散单体与用来制备第一种聚合物和均聚物的单体立构相异。

20. 制备权利要求12所述组合物的方法，包括：

a. 在催化剂存在下，将L-丙交酯或D-丙交酯单体与D,L-丙交酯单体相混合，并加热，其中L-丙交酯单体或D-丙交酯单体占85-95%（重量），D,L-丙交酯单体占15-5%（重量），最终形成一种均匀的溶液，

b. 聚合步骤(a)的溶液，

c. 处理步骤(b)形成的聚合物以改善其性质。

21. 按权利要求20的方法，所述处理是添加D-丙交酯或L-丙交酯共聚物进行共混。

22. 按权利要求20的方法，所述处理是添加成核剂和D-丙交酯或L-丙交酯聚合物进行共混。

23. 按权利要求20的方法，所述处理包括：

a. 添加链转移剂控制步骤(b)的聚合，

b. 添加成核剂和D-丙交酯或L-丙交酯均聚物进行共混。

24. 按权利要求20的方法，所述处理包括向该组合物添加附加的增塑剂这一处理步骤，所述增塑剂选自D-丙交酯、L-丙交酯、内消旋D,L-丙交酯、乳酸、丙交酯低聚物、乳酸低聚物和它们的混合物。

25. 按权利要求20的方法，选择单体时，至少一种单体要与选自步骤(a)的单体立构相异。

26. 使含有第一种可取向聚苯乙烯单元的热塑性聚合物组合物可在环境中生物降解的方法，包括：

用未取向时拉伸强度至少为5000psi，正切模量至少为200000psi，

且其中分散有0.1-5%（重量）增塑剂的第二种可取向聚合物代替聚苯乙烯单元，所述第二种聚合物含有下述聚乳酸单元：

$$\left(\!-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-O\!-\right)_n$$
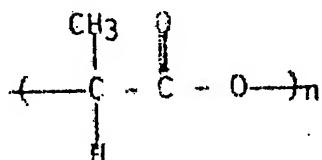
其中 n 是75-10000之间的整数， α-碳是L-构型和D-构型的混合物，其中D-构型单元偏多或L-构型偏多，该聚合物是由85-95%（重量）L-丙交酯或D-丙酯和15-5%（重量）D.L-丙交酯制备的。

2 7 ．一种可在环境中降解的组合物，包括下述各组分的机械混合物：

a．聚乳酸，

b．选自对苯二甲酸乙二醇酯聚合物、苯乙烯、乙烯、丙烯、氯乙烯、乙酸乙烯基酯、甲基丙烯酸烷基酯、丙烯酸烷基酯的聚合物或共聚物以及它们的机械混合物的聚合物。

2 8 ．按权利要求27的组合物，其中聚乳酸与所选的聚合物之重量比介于99:1至1:99之间。

2 9 ．制备权利要求27组合物的方法，包括：

a．提供聚乳酸，

b．从对苯二甲酸乙二醇酯聚合物，苯乙烯、乙烯、丙烯、氯乙烯、乙酸乙烯基酯、甲基丙烯酸烷基酯、丙烯酸烷基酯的聚合物或共聚物，及它们的机械混合物中选取聚合物。

c．共混步骤(a)和(b)的聚合物。

3 0 ．按权利要求27的组合物，其中含有选自D-丙交酯、L-丙交酯、内消旋D.L-丙交酯、乳酸、丙交酯低聚物、乳酸低聚物和它们的混合物的增塑剂。

7

31. 制备可在环境中降解的组合物的方法，包括：

a. 提供选自D-丙交酯、L-丙交酯、内消旋D,L-丙交酯、外消旋D,L-丙交酯和它们的混合物的丙交酯单体，

b. 从对苯二甲酸乙二醇酯聚合物、苯乙烯、乙烯、丙烯、氯乙烯、乙酸乙烯基酯、甲基丙烯酸烷基酯、丙烯酸烷基酯的聚合物或共聚物，及它们的机械混合物中选择一种聚合物，

c. 在足以熔融丙交酯和至少部分溶解所述聚合物的条件下混合及加热步骤(a)所选的丙交酯和步骤(b)所选的聚合物，

d. 聚合步骤(c)混合物中的丙交酯，得到聚丙交酯和所述聚合物的共混物。

32. 按权利要求31的方法，还包括：

e. 将上述共混物成型为自支承结构。

33. 按权利要求31的方法，其中包括监测剩余单体量，控制步骤(d)的聚合，以便得到含有剩余单体的共混物。

34. 按权利要求31的方法，还包括：

e. 聚合后向该共混物添加增塑剂，所述增塑剂选自丙交酯单体、丙交酯低聚物、乳酸低聚物、乳酸和它们的混合物。

35. 一种可在环境中降解的组合物，包括由下列各组分的机械混合物组成的共混物：

a. 聚乳酸，

b. 一种可以改善聚乳酸耐冲击性能的共混相容的聚合物。

36. 按权利要求35的组合物，其中聚乳酸占该组合物的50-99%（重量）。

37. 按权利要求35的组合物，其中共混相容的聚合物是嵌段聚酯。

38. 按权利要求37的组合物，其中共混相容的聚合物是聚对苯二甲酸丁二酯结晶硬链段与聚醚二醇长软链段的嵌段共聚物。

39．制备权利要求35的组合物的方法，包括：

a.提供聚乳酸，

b.选择可提高耐冲击性的共混相容聚合物，

c.共混步骤(a)和(b)的聚合物。

40．按权利要求39的方法，其中选用嵌段聚酯。

41．按权利要求39的方法，其中选用由聚对苯二甲酸丁二酯结晶硬链段和聚醚二醇长软链段组成的嵌段共聚物或天然橡胶和苯乙烯-丁二烯共聚物。

42．制备权利要求35的组合物的方法，包括：

a.将一种或多种选自D-丙交酯、L-丙交酯、D,L-丙交酯及其混合物的丙交酯与一种能够提供改善耐冲击性能的共混相容的聚合物相混合，

b.加热并将该共混相容的聚合物溶解在步骤(a)的丙交酯中，形成一种溶液，

c.聚合该溶液中的丙交酯。

43．按权利要求42的方法，包括通过熔融加工将上述组合物加工成有用的形式。

44．按权利要求42的方法，包括选用含有嵌段聚酯的共混相容的聚合物。

45．按权利要求42的方法，包括从由聚对苯二甲酸丁二酯结晶硬链段和聚醚二醇长软链段组成的嵌段共聚物、天然橡胶和苯乙烯-丁二烯共聚物或其混合物中选用共混相容的聚合物。

46．按权利要求35的方法，包括：

e.向该共混物中添加增塑剂，所述增塑剂选自丙交酯单体、丙交酯低聚物、乳酸低聚物、乳酸和它们的混合物。

源于丙交酯的可降解热塑性塑料

本发明的第一实施方案是关于L-丙交酯、D-丙交酯、D,L-丙交酯及其混合物的增塑聚合物，这种聚合物适于用来制备通常由非降解性塑料（如聚乙烯）制备的包装材料，还涉及制备柔韧膜和其它包装材料的方法及其独有的制品。本发明可用来制备可生物降解的制品，同时这些制品也具有常规塑料的特征。

本发明的第二实施方案是关于一种材料及其制备方法，这种材料可作为结晶聚苯乙烯（有时也称为可取向聚苯乙烯或OPS）的替代物。这种材料是OPS的补偿物，由能够在大约1年内在环境中生物降解的聚酯组成。这种材料是由聚合的乳酸组成的聚酯，由D-乳酸或L-乳酸与D,L-乳酸制备。确切的物理性能由上述两种聚合单体单元的比例、处理方式和某些辅助剂（在某些情况下）确定，以便满足作为OPS替代物的需要。例如，当L-乳酸/D,L-乳酸的比例大约为90/10时，所得的乳酸聚合物（PLA）是一种良好的热塑性塑料，透明、无色且非常硬挺，非常适于用来制备一次性（单程）塑料的薄膜、泡沫材料和其它热成型制品。PLA作为包装塑料用过之后，于环境中慢慢生物降解为无害的物质。这种无害处理可以缓和日益严重的塑料污染环境的问题。

本发明第三实施方案涉及将常规热塑性塑料与聚乳酸共混。这提供了新型的可于环境中降解的热塑性塑料。这种可在环境中降解的热塑性塑料可应用于许多领域。还涉及制备柔韧膜和其它包装材料的方法，其独有的制品。本发明可用来制备能于环境中降解同时又具备常规塑料特

征的制品。

本发明的第四实施方案涉及将可相容的弹性体与聚丙交酯共混。这提供了耐冲击的改性聚丙交酯，这种聚丙交酯可应用于许多领域，包括应用耐冲击改性聚苯乙烯的那些领域。还涉及制备包装材料的方法及其独有的制品。本发明可用来制备能于环境中降解的并且具备常规耐冲击塑料特征的制品。

由于大量废弃的塑料包装材料造成环境问题，所以需要可以在环境中生物降解的热塑性塑料包装材料。在美国，1987年塑料销售量为537亿磅，其中127亿磅被列为塑料包装材料。大量的塑料被废弃，变成塑料污染源，它们不仅大刹风景，而且还威胁着海洋生物的生命。估计每年因此而死亡的海鸟数目高达1-2百万只，海生哺乳动物的死亡数目高达100000。

与处理塑料包装材料相关的另一个问题是垃圾填埋场也正在日益缩小。据估计九十年代初大多数主要城市现有的用于处理固体废物的垃圾填埋场地将被用完。塑料废物中一般约含有3%（重量）或6%（体积）的固体废物。

常规塑料的另一个缺点是，它们归根结底是由石油制备的，因此将受到外国原油进口不稳定性的制约。较好的原料应该得自可再生的国内来源。

然而，有充分的理由使用包装材料。可迅速加工的装有特定量产品的漂亮包装能够产生一种动人的美感。这些包装可以保持清洁和贮存稳定性，还具有其它所需的性能，如以便观察内容物的透明性。这些已知的包装材料生产成本低，化学稳定性高。然而，正是这种稳定性使得这些塑料具有很长的寿命，以致一次性使用完毕之后，废弃的包装在环境中将在难以计算的长时间内存在。

已知乳酸聚合物和共聚物在某些情况下是一种独特的材料，因为它

11

们可以生物降解，具有生物相容性，而且是热塑性的。这些聚合物是良好的热塑性塑料，它们在动物体内通过水解可在数月至一年的时间内百分之百生物降解。它们在潮湿环境中几周后开始显示出降解现象，放置在土壤或海水中，一年左右即可消失。降解产物是乳酸、二氧化碳和水，这些产物都是无害的。

实际上是将乳酸转化为环化二聚体丙交酯，丙交酯是聚合反应的单体。乳酸可以通过发酵玉米淀粉或玉米糖浆之类的兼价原料而得到，也可以从乙烯之类的石油化学原料制备。丙交酯单体通常是通过催化熔融聚合（一种已知的制备塑料的通用方法）转化为树脂的。通过用中间体单体进行聚合，上述树脂成分可以有所变化。分子量很容易控制。可以改变组成以便得到特殊的性能。

在许多专利文献和出版物中已经公开了各种环酯（如乙交酯、丙交酯和内酯）的均聚物和共聚物。早期专利文献所公开的聚合乳酸、丙交酯或两者混合物的方法不能得到具有良好物理性能的高分子量聚合物。这些聚合物的制品经常是发粘的胶粘材料，物理性能不好。参见US1995970，US2362511和US2683136。US2668162首次提出使用纯乙交酯和丙交酯制备高分子量丙交酯均聚物和共聚物。丙交酯是乳酸的二内酯。当形成丙交酯时，释放出副产物水。丙交酯可以开环聚合为高分子量线型聚酯，无需复杂的缩聚方法。与均聚物相比，丙交酯和乙交酯的共聚物可以改善韧性和热塑性加工性能。采用中间体丙交酯可以制得具有优异物理性能的PLA均聚物和共聚物。US2668162公开了丙交酯和乙交酯的共聚物，这种共聚物是韧性而透明的，可冷拉，可牵伸，能将于210℃形成自支承膜。

在该专利和其它文献还公开了丙交酯的均聚和共聚物方法，用以制备强韧、可取向、硬挺的结晶聚合物，这种共聚物可加工成具有生物相容性可生物降解（有时称为可吸收）的纤维和替换装置。这些聚合物通

过水解作用慢慢消失。参见美国专利号2703316，2785987，3297033，3463158，3531561，3620218，3636956，3736646，3797499，3839297，3982543，4243775，4438253，4496446；欧洲专利申请0146398；国际专利申请WO 86/00533 和 Offenlegundsschrift 2118127。

其它一些专利提出将这些聚合物用于韧性外科手术元件，如生物医学紧固件、螺钉、穿钉、钉、骨板等。参见US3739773，US4060089和US4279249 。

利用生物活性物质与丙交酯和/或乙交酯均聚物和共聚物的混合物制备的控制释放装置业已公开。参见美国专利号3773919，3887699，4273920，4419340，4471077，4578384，4728721；Environmental Science and Technology，7(10)，955(1973)；第五届国际生物活性物质控制释放讨论会，会议记录(R.G.Sinclair，5.12 and 8.2，University of Akron Press，1978。)。丙交酯聚合物和共聚物的这些应用需要韧性或玻璃态材料，这种材料是可抛光的且没有显示出作为热塑性包装材料所需的物理性能。

现有技术中已经公开了丙交酯共聚物作为包装材料的若干应用。例如，上述专利US2668162 中的透明自支承膜是由丙交酯和乙交酯共聚物制备的。在US2703316 中，将韧性可取向的丙交酯聚合物作为成膜前体。已经公开了一种柔韧、强固、质脆或柔软的"包装纸"。然而，为得到柔顺性必须用挥发性溶剂润湿聚丙交酯，否则只能得到硬而脆的聚合物。要求丙交酯单体的熔点大于 120℃。L-丙交酯单体熔点为95℃，D,L-丙交酯熔点为 128℃。这是现有技术中改性丙交酯聚合物以获得柔顺性的具体实例。在US3021309 中，将丙交酯与 δ-戊内酯和己内酯共聚，以便改性丙交酯聚合物，得到韧性的白色结晶固体。其中只提到含己内酯与2,4-二甲基-4- 甲氧甲基-5- 羟基戊内酯的共聚物的柔性固体共聚物组合物，未得到丙交酯的组合物。US3284417 涉及制备聚酯的方

法，这种聚酯可用作增塑剂和制备弹性体和泡沫体的中间体。该专利未采用丙交酯，而是用基于7-9元环内酯（如 ε-己内酯）的组合物得到所需的中间体。未给出拉伸强度、模量和伸长率数据。US3297033 提出用乙交酯和乙交酯-丙交酯共聚物制备不透明材料，这种不透明材料取向后可制成适于用作缝合线的纤维。其中写到"增塑剂阻碍结晶，但可用于海绵体和膜"。在这些公开内容中可以明显看到，除非进行增塑，否则上述交酯均聚物和共聚物是脆硬的。US3736646 也是这种情况，其中丙交酯-乙交酯共聚物是用二氯甲烷、二甲苯或甲苯之类的溶剂进行软化。在US3797499 中指出，L-丙交酯和D,L-丙交酯共聚物具有更大的柔韧性，可用于拉制用作可吸收缝合线的纤维。这种纤维强度大于50000psi、伸长率约为20%，模量约为1000000psi。与最柔韧的的包装材料组合物相比，这些纤维仍然是相当脆硬的，这与其作为缝合线的用途有关。US3844987 公开了利用可生物降解聚合物与自然存在可生物降解产物（如纤维素材料、大豆粉、谷壳、啤酒厂发酵粉）的共混物和接枝聚合物制备某些制品，如用来盛装促进种子或籽苗发芽和生长的介质的容器。这些制品不适于用作包装材料。

US4620999公开了一种制备可生物降解的一次性塑料袋的组合物，它含有3-羟基丁酸聚合物和3-羟基丁酸／3-羟基戊酸共聚物。大家都知道乳酸是2-羟基丙酸。US3982543 提出用挥发性溶剂作为增塑剂对丙交酯共聚物进行增塑，以得到柔顺性。US4045418 和US4057537 是通过将己内酯与丙交酯（L-丙交酯或D,L-交酯）共聚而获得柔顺性。US4052988 利用聚（对-二噁烷酮）〔poly（p-dioxanone)制备可吸收缝合线的扭结和扭结保险。US4387769 和US4526695 公开了只有在较高的温度才比较柔顺的丙交酯和乙交酯的聚合物和共聚物。欧洲专利0108933 采用由聚乙二醇改性的乙交酯共聚物获得一种三元嵌段共聚物，据称可作为缝合线材料。如上所述，有一点是一致的；即只有采用短效挥发性溶剂增

塑剂或其它共聚单体才能使丙交酯聚合物具有柔顺性。

L-丙交酯和D,L-丙交酯的共聚物在现有技术中是已知的，但引用的文献表明柔顺性并不是内在的物理性质。US2758987 公开了L-丙交酯或D,L-丙交酯的均聚物，据说可以熔融压制成透明强韧的取向膜。聚L-丙酯的性能如下：拉伸强度29000psi，伸长率23%,拉伸模量710000psi。聚D,L-丙交酯的性能为：拉伸强度26000psi，伸长率48%，拉伸模量260000psi。仅公开了重量比为50/50 的L-丙交酯和D,L-丙交酯的共聚物，即L-乳酸和D,L-乳酸的共聚物。只给出了粘点性质（实例3）。据称采用一种对映体单体（如光学活性的L-丙交酯）有利于获得高强度。US2951828 介绍了L-丙交酯和D,L-丙交酯均聚物以及重量比为75/25 、50/50 和25/75 的L-丙交酯/ D,L-丙交酯共聚物，其中公开了 a- 羟基羧酸的成珠聚合法。所得共聚物的软化点为 110-135℃。未给出与硬度和柔顺性有关的数据，只是给出了有关珠粒尺寸和软化点的数据。在US3636956 和US3797499 中提到了重量比为95/5、92.5/7.5、90/10 和85/15 的L-丙交酯/ D,L-丙交酯共聚物。评价其牵伸纤维长丝的性能，其拉伸强度大于50000psi，模量约为1000000psi，伸长率约为20%。和上述US3636956 一样，用增塑剂提高柔性。Offenlegundsschrift 2118127 公开了一种雪白色的明显结晶的聚合物，包括90/10 L-丙交酯/ D,L-丙交酯共聚物。但未给出此共聚物的物理性能。该专利指出所述材料可用于外科手术器件。

US3297033、3463158 、3531561 、3636956 、3736646 、3739773 和3797499 公开了丙交酯聚合物和共聚物，它们是适用于纤维和缝合线材料的具有强烈结晶倾向的可取向聚合物。这些公开内容介绍使用高结晶度的材料，通过牵伸和退火将此种材料取向，得到拉伸强度和模量分别大于50000psi和1000000psi的取向材料。虽然提到可以模塑成各种成型制品，但没有提到未取向挤出物和模塑品的物理性能。例如，

US3636956公开了制备90/10(重量) L-丙交酯/ D,L-丙交酯，以及牵伸取向纤维的方法。然而，上述文献提出最好采用纯L-丙交酯单体，以便提高结晶度和牵伸纤维的强度。

US3797499公开了一种95/5（重量）L-丙交酯/ D,L-丙交酯的共聚物（例Ⅴ），然而这种材料是用来制备长丝的。在第5栏第1行给出的性能不如本发明的相应性能，其中采用了甘油三乙酸酯、苯甲酸乙酯和邻苯二甲酸二乙酯之类的增塑剂。

US3736646、3773919、3887699、4273920、4471077和4578384公开了用丙交酯聚合物和共聚物作为载体药物释放的基质，它可以生物降解，而且是生物相容的。其中没有提到由普通热成型方法（如薄膜挤出或模塑法）制备的聚合物材料的物理性能。

特别令人感兴趣的是US4719246，其中公开了共混L-丙交酯均聚物、D-丙交酯均聚物、它们的混合物或聚合物和L-丙交酯或D-丙交酯与至少一种非交酯共聚单体的共聚物的方法。这种共混方法旨在制备含有互相作用的聚L-丙交酯链段和聚D-丙交酯链段的组合物。

加拿大专利第808731号公开了一种L-丙交酯和D,L-丙交酯的共聚物，其链结构中含有Ⅱ族二价金属。据称该90/10 L-丙交酯/ D,L-丙交酯共聚物（实例2)和L-丙交酯均聚物适用来制膜和纤维。该90/10共聚物是雪白颜色的共聚物，L-丙交酯均聚物可制成透明膜（聚合物结晶度越高越不透明，或为雪白色的均聚物材料），该专利中写到"本发明新型聚丙交酯中含有以乳酸盐形式存在的金属催化剂组分这一事实具有重要意义"，"所述聚丙交酯可用常规热塑性树脂加工方法制成膜和纤维"。但未给出膜的强度和柔韧性等物理性能的数据。

加拿大专利第863673号公开了L-丙交酯和D,L-丙交酯共聚物的组合物，其中L-丙交酯与D,L-丙交酯的比例分别为97/3、95/5、92.5/ 7.5、90/10和85/15。这些组合物的特征是可作为外科应用的牵伸长丝。拉

伸强度很高，约为100000psi，伸长率约为20%。其中提到使用增塑剂增加柔性。权利要求中提到的是百分重量小于15的D,L-丙交酯组合物。

加拿大专利第923245号公开了L-丙交酯和D,L-丙交酯的共聚物（实例15）。据称该90/10共聚物是雪白颜色的聚丙交酯。据称可用常规热塑性树脂加工方法将该聚丙交酯制成膜和纤维。

US4719246公开了一种共混聚L-丙交酯、聚D-丙交酯、两者混合物的聚合物和L-丙交酯或D-丙交酯与至少一种非丙交酯共聚单体的共聚物的简便方法。给出的例子都是机械混合物。其特殊的"互锁"性能是因为形成了外消旋化合物（"碳化合物立体化学"，E.L.Eliel，McGraw-Hill，1962，P.45）。外消旋化合物由"互锁"对映体组成，即D型和L型（或R型和S型），彼此靠极性力互相吸引。这可以使得结晶熔点上升或下降，视D与D（或L与L）之间的力和D与L之间的力相对大小而定。为增强这种效应所需的外消旋聚合物组合物（参见US4719246，第4栏，第48行）应采用D和L均聚物或长分子链。这种结构的高度对称性或规整性使得它们能够用很强的极性力彼此吻合或互锁，还因为它们是相同的或互成镜像。这导致了强烈的结晶倾向。外消旋化合物技术具有很长的历史，可以追溯到经典化学。

US4661530公开了一种聚L-乳酸和/或聚D,L-乳酸和嵌段聚酯氨基甲酸酯或聚醚氨基甲酸酯的混合物，由此混合物制成的生物降解材料可用作外料整形技术中生物组织和器官的合成替代物。

现有技术中从未公开过用丙交酯单体、乳酸和乳酸或丙交酯的低聚物作增塑剂的丙交酯聚合物可制成柔顺的具有高度延展性的组合物。上述现有的组合物均不适用于热塑性聚合物包装材料。

本技术领域的技术人员都理解，将一种热塑性塑料的性能与另一种热塑性塑料的性能相叠加，结果是不可预料的。例如，就结晶聚苯乙烯或OPS而言，非常需要这种聚乙烯具有满意的性能，而聚苯乙烯已经开

发了许多年，以满足加工和最终使用不同等级OPS的需要。

本发明的一般概念和第一实施方案是，L-丙交酯均聚物、D-丙交酯均聚物、D,L-丙交酯均聚物和它们的单体混合物的共聚物，它们用丙交酯单体、乳酸、丙交酯低聚物或乳酸低聚物增塑可以象性能良好的热塑性塑料一样应用，它们可以模拟通常在环境中不能降解的塑料（如聚乙烯等）的性能。这种组合物的聚合物具有如下通式

$$\left(\underset{\underset{H}{\overset{\alpha}{\underset{|}{\overset{|}{C}}}}}{\overset{\overset{CH_3}{|}}{C}} - \overset{\overset{O}{\parallel}}{C} - O\right)_n \qquad\qquad I$$
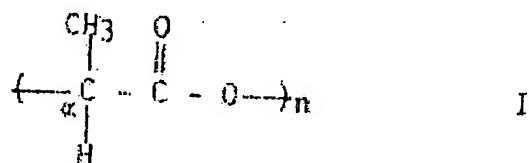
并且是用选自丙交酯、乳酸、乳酸低聚物及其混合物的增塑剂增塑的。乳酸低聚物最好如式Ⅱ所示

$$\left(\underset{\underset{H}{\overset{\alpha}{\underset{|}{\overset{|}{C}}}}}{\overset{\overset{CH_3}{|}}{C}} - \overset{\overset{O}{\parallel}}{C} - O\right)_m \qquad\qquad Ⅱ$$
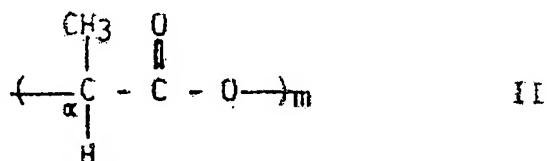
式中 m 为整数，且 $2 < m < 75$，最好 $2 < m < 10$。增塑剂最好占聚合物的2-60%（重量）。所述聚合物可由选自L-丙交酯、D-丙交酯、内消旋D,L-丙交酯及其混合物的丙交酯单体制备。n 为整数，且最好 $150 < m < 20000$。

丙交酯单体含量为聚合物的5-40%（重量），而丙交酯低聚物或乳酸及其低聚物的含量为2-60%（重量）。这种组合物具备许多所需的聚乙烯的性质，如柔顺性，透明性和韧性。

另外还提供了一种制备该可生物降解组合物的方法。该方法包括：混合，加热和熔融一种或多种丙交酯单体及催化剂；聚合上述单体溶液形成聚合物，聚合温度要足够低，以便使聚合尚未完成时即可停止，监

测单体含量，在聚合完全之前剩余单体达到一定量时停止反应，从而使未反应的单体截留在聚合物中。

还提供了一种制备聚乳酸增塑聚合物的方法，包括：混合，加热和熔融一种或多种丙交酯单体及催化剂；聚合上述单体溶液形成聚合物，中途不停止反应；向该聚合物中添加增塑剂。所述增塑剂选自D-丙交酯、L-丙交酯、内消旋D,L-丙交酯、乳酸、乳酸低聚物和它们的混合物。

本发明的第二实施方案包括一种制备可在环境中生物降解的组合物的方法和适于用作聚苯乙烯替代物的可在环境中生物降解的组合物。所述组合物含有式I的聚乳酸单元（其中n为整数，75<n<10000，α-碳是L构型和D构型的混合物，D构型偏多或L构型偏多），其中的聚合物是由L-丙交酯或D-丙交酯(85-95重量份)和D,L-丙交酯（15-5重量份）制备的，未取向时该聚合物的拉伸强度至少为5000psi，正切模量至少为200000psi，其中分散有0.1-5%（重量）的增塑剂。

本发明的第三实施方案是提供一种制备可在环境中降解的组合物的方法，和含有聚乳酸与一种或多种选自对苯二甲酸乙二醇酯聚合物，苯乙烯、乙烯、丙烯、氯乙烯、乙酸乙烯基酯、甲基丙烯酸烷基酯、丙烯酸烷基酯的聚合物或共聚物及其物理混合物的共混物的环境中降解组合物。

本发明的第四实施方案是提供一种制备可在环境中降解的组合物的方法和一种可在环境中降解的组合物。该组合物包括聚乳酸和能够改善冲击性能的共混相容弹性体的物理混合物的共混物。例如，这种弹性体可以是Hytrel，即聚对苯二甲酸丁二酯结晶硬链段和聚醚二醇长软链段的嵌段聚合物之类的嵌段聚酯。商品名为Hytrel4056（杜邦）的嵌段聚酯是一个已知实例。

图1是表示组合物中作为增塑剂的丙交酯百分含量与拉伸强度关系的曲线。

图2 是表示组合物中作为增塑剂的丙交酯百分含量与弹性模量关系的曲线。

图3 是表示组合物中作为增塑剂的低聚物百份含量与拉伸强度关系的曲线，其中曲线A 代表90/10 共聚物，曲线B 代表92.5/7.5共聚物。

图4 是表示组合物中作为增塑剂的低聚物百分含量与弹性模量关系的曲线，其中曲线A 代表90/10 共聚物，曲线B 代表92.5/7.5共聚物。

图5 是实例5B未退火的90/10 L/D,L-丙交酯共聚物的示差扫描量热（DSC）曲线。

图6 是实例5B的材料于70℃放置 100分钟后的DSC 曲线。

图7 是实例5B的材料于 185°F 退火过夜后的DSC 曲线。

图8 是混有5%乳酸钙的实例5B材料的DSC 曲线。

图9 给出聚苯乙烯和实例8B制备的丙交酯聚合物的熔融粘度和剪切速率的对比数据。

图10是实例8B共聚物的DSC 曲线。

图11是添加到实例8B共聚物中的L-丙交酯均聚物的DSC 曲线。

图12是含有实例8B共聚物和L-丙交酯均聚物的实例23的共混组合物的DSC 曲线。

图13是混有5%（重量）聚苯乙烯的90/10 L-/ D,L-丙交酯共聚物的DSC 曲线。

第一通用实施方案

本文所公开的可在环境中生物降解的组合物能够完全降解为环境可接受的相容的材料。降解的中间产物，即乳酸和乳酸或丙交酯的短链低聚物是自然界广泛存在的物质，这些物质易于被各种微生物所代谢。它们的天然最终分解产物是二氧化碳和水。通过适当选择材料，这些组合物的预期等同物（如含有少量其它材料、填料或增量剂的组合物）也可以在环境中完全降解。上述组合物提供了环境上可接受的材料，因为与

20

由它们替代的常规非降解性塑料相比，它们物理退化和降解过程要快得多并完全。此外，因为此组合物的全部或主要部分是聚乳酸和/或由乳酸衍生物的丙交酯和低聚物，所以没有或只残留有少量降解速率较慢的物质。这种残留物比降解速率较高的本体产物具有更大的表面积。

一般应用本发明导致了本发明的第一通用实施方案。D-丙交酯、L-丙交酯、D,L-丙交酯的均聚物和D-丙交酯与L-丙交酯的共聚物，L-丙交酯与D,L-丙交酯的共聚物，D-丙交酯与D,L-丙交酯的共聚物与D-丙交酯、L-丙交酯和D,L-丙交酯的共聚物，在用丙交酯单体、乳酸、丙交酯低聚物、乳酸低聚物和它们的混合物增塑后，均可制成适用于本发明的材料。增塑剂可以通过在聚合尚未完全时终止反应而形成。可任选补加到聚合物中的附加增塑剂，包括丙交酯单体（D-丙交酯，L-丙交酯，D,L-丙交酯或它们的混合物），乳酸、乳酸或丙交酯低聚物和它们的混合物。上述聚合物由式I定义：

$$\left[\begin{array}{c} CH_3 \\ | \\ -C \\ | \\ H \end{array} \begin{array}{c} O \\ || \\ -C-O- \end{array}\right]_n \qquad I$$
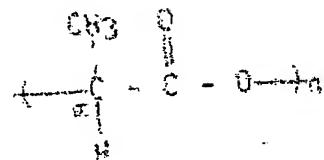
式中 n 代表聚合度（重复单元数）。所述聚合物是由其不完全聚合所残留的单体增塑剂增塑的。增塑剂越与该聚合物一体化，性能越好。如果需要，可以向残留在组合物中的单体或低聚物补加附加的单体或低聚物。可用作增塑剂的乳酸低聚物由式II定义：

$$\left[\begin{array}{c} CH_3 \\ | \\ -C \\ | \\ H \end{array} \begin{array}{c} O \\ || \\ -C-O- \end{array}\right]_m \qquad II$$
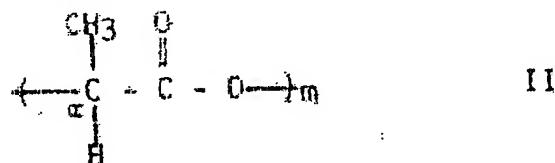
式中m 是整数，且 $2 < m < 75$，最好 $2 < m < 10$。

L-丙交酯、D-丙交酯和D,L-丙交酯的比例对获得柔顺的热塑性塑料并不重要。L-丙交酯、D-丙交酯和D,L-丙交酯的组份可在很大范围的重量比例变化，以制成均聚物或共聚物。在本发明方法中使用的丙交酯单体可从市场购得，这样就不必用单体反应物本身，也不用本发明的制备方法来制备。

D-丙交酯是D-乳酸的二内酯或环状二聚体。类似地，L-丙交酯是L-乳酸的环状二聚体。内消旋D,L-丙交酯是D-和L-乳酸的环状二聚体。外消旋D,L-丙交酯包括D-和L-丙交酯的混合物。当在此单独使用术语"D,L-丙交酯"时，它是指包括内消旋D,L-丙交酯或外消旋D,L-丙交酯。

在文献中记录的制备丙交酯的方法之一是在高真空下将乳酸脱水。产物在高温和低压下蒸馏。丙交酯及其制备方法在下列文献中讨论：W.H.Carothers，G.L.Dorough和M.J.Johnson（J.Am.Chem.Soc.54,761-762〔1932〕），J.Gay-Lussac 和J.Pelouse（Ann，7,43〔1833〕）；C.A.Bischoff和P.Walden（Chem.Ber.26,263〔1903〕；Ann.279.171〔1984〕），和Heinrich Byk（Ger.Pat.267,826〔1912〕）；及Chem.Abstr.8,554,2034〔1914〕）。

光学活性酸可利用各种细菌属Lactobacillus，如Lactobacilus delbrueckii，L.Salirarius，L.casei等等直接发酵几乎任何无毒碳氢化物，付产物或废物来制备。光学活性酸也可以用锌铵盐类或生物碱如吗啡的盐来拆开外消旋混合物来制备。L-丙交酯是分子量为 144的白色粉末。如果从市场购得不纯的L-丙交酯用于本发明，较好的是用无水甲基异丁基酮来重结晶纯化。雪白色L-丙交酯晶体的熔点为96- 98℃。

用于制备D,L-丙交酯的D,L-乳酸是可购得的。D,L-乳酸可用合成法制备，将乳腈（乙醛合氰化氢）水解，或用各种细菌属Lactobacillus直接发酵几乎任何种无毒碳氢化物，付产物或废物来制备。D,L-丙交

是分子量为 144的白色粉末。如果在本发明中使用市场购得的不纯产物，可用无水甲基异丁基酮重结晶纯化。将这种含有在90-130℃温度下熔融的泥煤半固体物的市售产物用甲基异丁基酮重结晶，再用木炭脱色。这样重结晶三次后，产物在真空、氮气流和室温下转动干燥8-24小时。这样制得的雪白色晶体包括D,L-丙交酯混合物，熔点为 115-128℃。

按照本发明方法制备组合物时，较好的是在密闭高压釜中，在有至多18个碳原子的羧酸锡酯存在下，液相反应而进行。组合物也可以是大气压下、用惰性气体如氮气保护下的聚合反应来制备。如果聚合反应是在氧气或空气下进行的，则要有脱色，这样就使得分子量和拉伸强度下降。该方法是在这样的温度下进行的，使聚合反应在它的后期进行缓慢，使残留单体截留在粘滞的聚合物熔体中。可达到这一目的的较好温度一般在纯L-丙交酯的熔点至纯D,L-丙交酯的熔点之间，即在95-127℃。目前认为在约 129℃温度下，这不会对本发明的范围有限定的，可发生下列情况：

1．L-和D,L-丙交酯单体的丙交酯单体混合物熔融形成低共熔的混合物。该混合物熔融成一种可流动的流体，它是一、二或三种单体的均匀溶液。

2．流动的熔体催化聚合成较高粘度的溶液，最终未反应的单体截留在聚合物中，成为溶液而不是分散均匀相。因为反应很容易分散控制，并且不能接触到低含量的聚合物活性端基，单体不再进行反应。

3．聚合反应停止或大大减慢，这样在室温下，单体和聚合物的共混物成为固体溶液，使组合物具有塑性、透明和柔韧。

4．催化剂失活，这样在以后的熔融制备中不能促进聚合反应。

5．塑化的组合物是非常稳定的，因为残余的单体具有非常高的沸点如丙交酯的沸点是 8毛下 142℃，并且与它的开链互变体密切相关。

另外，该方法可在L-丙交酯的熔点至 200℃温度下进行，然后乳酸

或丙交酯熔融或溶剂共混成用于下步的聚合物。不希望温度高于 200℃，因为使共聚物易于降解。在95-200℃温度内升高温度通常可提高聚合反应速度。在约 110℃-160℃温度下加热L-丙交酯和D,L-丙交酯的混合物可获得好的结果。

本发明所用催化剂是含有至多18个碳原子的羧酸锡酯。这类酸的实例是甲酸、乙酸、丙酸、丁酸、戊酸、己酸、辛酸、壬酸、癸酸、月桂酸、十四烷酸、十六烷酸、硬脂酸和苯甲酸。用乙酸亚锡和辛酸亚锡可得好的效果。

催化剂是按常用催化剂量来使用。一般来讲，催化剂用量为L-丙交酯和D,L-丙交酯总重的约0.01-2%（重量）。较好的催化剂用量为约0.01-1.0%（重量）。最好的催化剂用量约为0.02-0.5%（重量）。在具体情况下，催化剂的精确用量很大程度上取决于所用催化剂、加工条件包括时间和温度。准确的条件本专业技术人员是很容易确定的。

聚合反应步骤本身的反应时间是由其它反应条件所控制的，反应条件包括反应温度、特定催化剂、催化剂用量和是否使用液体载体。根据具体实例所用反应条件，反应时间可从几分钟至几小时或几天变化。将单体的混合物连续加热直到测定出聚合反应达到所要求程度。聚合反应的程度可通过分析残留单体来确定。正如前面讨论的，可选定反应温度来提高单体的掺入量，并由聚合反应器中直接得到塑化的组合物。当单体转化为聚合物的转化率达到所要求的程度，获得的组合物具有所需的塑化性时，反应停止。在本发明较好的实施方案中，根据所要求的塑化程度，大约2-30% 丙交酯没有发生反应。

一般来讲，在进行聚合反应时较好的是不存在含有活泼氢的杂质，因为这种杂质存在使得催化剂失活和/ 或增加了诱导时间。进行聚合反应较好的是在基本上无水的条件下完成。

本发明的共聚物较好的是本体聚合、悬浮聚合或溶液聚合来制备。

聚合反应是在有惰性的、常态下是液态的有机载体存在下进行，该载体例如有芳香烃如苯、甲苯、二甲苯、乙基苯等等；氧化的有机化合物如苯甲醚、1,2-亚乙基二醇的二甲酯和二乙酯；通常为液态的饱和烃包括开链、环状和烷基取代的环状饱和烃如己烷、庚烷、环己烷、烷基环己烷、十氢化萘等等。

聚合反应过程可以分批、半连续或连续进行。在制备用于以后的聚合反应的丙交酯单体反应物和催化剂时，可将它们按照已知聚合方法的任何方法来掺和。这样，催化剂可加到任一种单体反应物中。此后，含有催化剂的单体可与其它单体掺和。另一种方法是 单体反应物彼此掺和，然后将催化剂加入到反应混合物中。如果需要，可将催化剂溶解或悬浮在惰性的、常态下为液态的有机载体中。如果需要，也可以将单体反应物以惰性有机载体的溶液或惰性有机载体的悬浮液加入到催化剂、催化剂溶液或催化剂悬浮液中。还有，催化剂和单体反应物可以一起加入到反应釜中。反应釜可以装有常用热交换器和/或混合装置。反应釜可以是制备催化剂技术中所用的任何常用设备。例如，不锈钢釜是适用的反应釜。

由本发明制备的在环境中生物降解的组合物，按照L-丙交酯、D-丙交酯、内消旋D,L-丙交酯的不同比例可用于制造制品中，例如薄膜、纤维、模制品和层压制件，这些制品可由常用制造方法制备。这些制品可以非医用，既体外使用，在此它们可以代替常用非环境降解塑料。

例如，丝可通过喷丝嘴熔融挤出共聚物来制成。薄膜的制备如下，将生物降解组合物的溶液浇铸，然后除去溶剂，也可以用带有加热压板的液压机来压制固态生物降解组合物，或通过模头挤出。

可使用各种方法如慢速冷却和快速冷却来由本发明的共聚物制备模制品。

本发明组合物的预期等同物是含有少量其它物质的组合物。如果需

要，本发明制备的共聚物可通过加入交联剂、增塑剂、着色剂、填料等等来改性。

交联作用是将组合物与游离基引发剂如氢过氧化枯烯化合，然后在较高的温度下模制而进行的。这样可改善耐热性和耐溶剂性。固化也可以这样进行的，共聚物与多官能化合物如多元醇化合并模制，或在加热和真空下热成形。为进行聚酯固化的接枝—挤出反应是使共聚物交联和链增长的显而易见方法。

在制备模制品时，固化之前可向组合物加入填料。填料可改善模制品的性能，包括硬度、强度、热温性等等。已知的填料包括铝粉、碳酸钙粉末、硅石、高岭土（粘土）、硅酸镁等等。最好的填料是淀粉，它可与组合物充分共混以制得可完全环境生物降解的共混物。其它性能的改善可通过将组合物与丙交酯、乙交酯和己内酯的其它聚合物和共聚物熔融共混而获得。

本发明的组合物可按照已知方法制成增强层压制品。通常，层压制品的制备是，纤维簇或多层片材成型成的基体固结成单元结构，固结是将熔融前体或组合物流入到纤维材料，并且在模具中或液压固化制成聚合物。在制备基体时所用纤维包括天然和合成纤维如木头、棉花、亚麻线、大麻等的纤维素，玻璃、尼龙、乙酸酯纤维素等等。

本发明的组合物及其制备通过下列具体实例来进一步说明。

实例1

80/20,L-丙交酯/ 外消旋D,L-丙交酯

将均为高纯度的 160克L-丙交酯和40克外消旋D,L-丙交酯(Purac公司出产、三重结晶）装到 500毫升圆底烧瓶中，吹入干燥氮气过夜。将10毫升辛酸亚锡溶解在60毫升无水甲苯中，将10毫升溶剂蒸馏到迪安-斯达克榻分水器中，以便通过共沸点蒸馏作用将这种催化剂溶液干燥。从10毫升辛酸亚锡的50毫升无水甲苯溶液中，用注射器取出 0.2毫升份，注入到在反应烧瓶内的丙交酯中。继续用注射器针头吹入氮气，该注射器针通过橡胶隔膜和鼓泡器相连的一段管道的出口相连，并通入反应烧瓶。氮气流量保持在每秒1-3 个气泡。烧瓶在油浴中加热至 123~127℃。在第一步加热中，丙交酯熔融并通过摇振将其充分混合。此后，产物变得非常粘稠。加热20小时后，将烧瓶和无色、透明的产物从加热浴中移出，冷却，打碎烧瓶，用液态氮冲洗以除去产物中的玻璃。该共聚物用加热液压机模塑。在20,000磅压下和 170℃温度下于 2分钟内可压塑成5-10密耳厚薄膜。用Instron 试验机测定薄膜的拉伸性能，结果列在表1。还要模塑成 1/8英寸厚试样用于冲击强度试验。对产物进行热失重分析(TGA)，记录将试样于 4分钟内加热到 150℃并在 150℃保持60分钟后重量的损失。试样的失重为19.5% ，并60分钟后基本上不再继续失重。失重是由于丙交酯单体损失造成的。差示扫描量热法(DSC) 的结果表明组合物在约 110℃开始吸热，随着温度升至 200℃，曲线变得更加弯曲。没有观察到熔点。试样在 135°F 温度下退火过夜，并重新测试。它们仍是透明的、无色和柔韧的。可将共聚物试样重复模塑6 次，而没有变色或明显的强度损失。尽管反复模塑，薄膜仍是透明、无色和非常柔韧的。

表1　当用丙交酯增塑时L-丙交酯和D,L-丙交酯的共聚物[a]的性能

实例号	1	2	3
膜厚度　密耳	8	8	8
拉伸强度　1000psi ASTM D638	3.9	1.7	7.9
伸长率　%	28	806	3.5
100%模量　1000psi	0.74	—	
200%模量　1000psi	1.20	—	
正切模量　1000psi	36.6	—	289
缺口冲击强度　英尺-磅/英寸[b]	0.63	—	0.4
Mw，×1000	540	281	341
Mn，×1000	270	118	97.5
残留丙交酯[c] %	19.5	27.8	2.7

(a) L-丙交酯/ D,L-丙交酯的重量比为80/20

(b) 1/8 英寸，缺口试样

(c) 在 150℃温度等温TGA 失重

实例2

在 3升圆底烧瓶中装入1.84千克L-丙交酯、0.46千克外消旋D,L-丙交酯和 2.3毫升辛酸亚锡溶液，与实例1相似。向该混合物通入氮气 3小时，然后在 125℃油浴中等温加热。该混合物熔融，摇振下充分混合，制成了均匀、透明、无色流体。几小时后，该流体的粘度实质上提高了。64小时后，将烧瓶从加热浴中取出，冷却，并从清彻透明的固体产物中除去玻璃碎片。橡胶态组合物切成薄片，在研磨机中与干冰一起研磨成 1/8英寸或更小粒度。研磨物在 100°F 的空气循环烘箱中干燥几小时，然后在室温下真空干燥过夜。按照实例 1所述制备压塑薄膜，并测定薄膜的拉伸性能和TGA 失重，列于表1。

实例3

在 250毫升圆底烧瓶中装入 79.98克L-丙交酯、 20.04克外消旋D,L-丙交酯和0.20毫升辛酸亚锡溶液，类似于实例1。将氮气吹入烧瓶中，并在 125℃油浴中加热。将该混合物熔融成为无色可流动的液体，摇动烧瓶来充分混合该液体。 2小时后，油浴温度升至 147℃，总共加热14小时。产物是透明、无色的玻璃态。经过测定与上述实例类似，结果列于表1。

实例1 至3 说明了反应温度对所得组合物中共聚物性能的影响。

实例4

将实例1 和实例3 的共聚物膜浸在水中几个月。 3个星期后，实例1 的共聚物变模糊了，而实例3 的共聚物在约 2个月仍然透明，3个月后，实例3 的薄膜变得明显模糊，而实例1 的薄膜为白色并不透明。与实例1 接触的水尝起来为酸的，而与实例3 的薄膜接触过的水无味。

表1 数据的研究表明实例1 的共聚物是在环境中生物降解的并可代替聚乙烯。本技术领域技术人员不难看出在许多种包装应用中，上述共聚物的综合物理性能是优异的。在例如塑料垃圾箱、通用包装薄膜、塑料购物袋、多层包装纸、包装带等等的应用中，它们的拉伸强度和初始正切模量比起聚乙烯组合物要优异的。该共聚物和常用于垃圾箱组合物的线型低密度聚乙烯组合物的应力－应变曲线的形状大致相同。性能的比较列于表2。

表2　聚乙烯与聚乳酸聚合物的比较

性能		LDPE[a]NA272	LLDPE[b]	丙交酯共聚物[c]
拉伸强度	1000psi	2.18	2.9	3.90
ASTM标准C				
伸长率 %		216	500	280
正切模量	1000psi	54.9	51.0	36.6

100%模量	1000psi	1.77	–	0.74
200%模量		1.82	–	1.20
HDT[d]	264psi.F	95	99	122

(a) 在本实验中的线型低密度聚乙烯，5-10密耳，2英寸/分钟。

(b) 线型低密度聚乙烯，由计算机资料得到数据。

(c) 实例1 的L-丙交酯/ D,L-丙交酯共聚物。

(d) 热变形温度。

在可控制的工艺中，上述丙交酯聚合反应可在单体尚未完全转化为聚合物时停止。这在实例1和2说明了。丙交酯单体与丙交酯聚合物粘结的非常紧密。另外，该组合物也可由丙交酯与预制聚合物混合来制备。在这种情况下，加入的丙交酯的立体化学构型可相同或不同，即L-、D-或D,L-丙交酯，以用来制备聚合物。

混合过程是将熔融聚合物与丙交酯单体在常用加工设备如原纸辊或双螺杆混炼机中共混而进行。将常用硬挺、玻璃态丙交酯聚合物用丙交酯增塑，并仍然保持透明、无色和基本上无味。丙交酯并不是很不稳定的，需要加热和氮气吹扫，一般为 170℃-200℃温度下 20-60分钟，以除去重量分析中的丙交酯。在光学显微镜下，不能看到薄膜中有丙交酯。丙交酯区域结构在尺寸上属亚微观级。这种聚乳酸的韧柔性可使它用作为可环境生物降解的替代物，来代替一次性使用的聚烯烃包装膜。

实例15-16：

一系列的试验是这样进行的，制备L-和外消旋D,L-丙交酯共聚物，与各种量的丙交酯熔融共混，测定作为丙交酯组合物含量的函数的共混物的物理性能。丙交酯单体含量是由已知的等温、热重分析（TGA）法来测定。丙交酯含量是在混合和模塑成薄膜之前和之后测定的。

据观察，开辊、两辊研磨使得丙交酯在非常高分子量丙交酯共聚物所需温度下挥发。这种损失可通过炼胶或采用低分子量丙交酯共聚物

（以及与它们相应的较低混合温度）来减少。较好的混合和共混方法是用贯用双螺杆挤出机，这样可减小挥发的损失。某些结果列于表3。聚丙交酯和丙交酯增塑剂的共混物是非常柔韧的，并随着丙交酯含量的增加而提高。它们是无色和透明的。仅能测到非常弱的丙交酯气味（较好的），并不可明显地辨别出是丙交酯味。表3 的增塑薄膜试样是抗撕裂性的、易折叠的并可刺孔而不破碎或撕裂。当放在冰箱(5℃，40°F)中时，它们是有些硬的。但仍然柔韧并可折叠而不破碎。这种薄膜手感非常软，玻璃化温度低于37℃。当丙交酯含量低于20% 时，该薄膜运动时具有典型的聚烯烃薄膜那种喀啦声。当丙交酯含量较大时，薄膜具有聚氯乙烯的褶皱性和"暖"感。

如表3 所示，弹性模量（初始正切模量）可相当高，类似于线型低密度聚乙烯(LLDPE)。这表明它们的状态稳定。低的模量和拉伸强度与低密度聚乙烯(LDPE)相似。作为丙交酯含量的函数的物理性能描绘在图1 和2 中。关于表3，在大约 7-20%的丙交酯含量时，拉伸性能与用于垃圾箱和购物袋的聚乙烯相似。

在较低丙交酯含量时，共混物与聚丙烯相似。有些数据与表3 相比较。表4 说明了用于对比的普通塑料。

表 3： 增塑PLA(a)组合物的拉伸性能比较

实例号	组合物	丙交酯 %,TGA	弹性模量 1000 psi	1%割线模量 1000 psi	屈服强度 1000 psi	流动性 极限 %	破裂强度 1000 psi	破裂时应变 %
5	90/10, L-/D,L-丙交酯共聚物	1.3	289	291	0	0	7.5	3
6	"	17.3	119	119	2.23	4	2.29	288
7	"	19.2	95.5	90.3	1.97	5	4.24	536
8	"	19.6	88.7	88.7	1.72	4	2.12	288
9	"	20.5	50.3	50.3	1.21	5	2.16	338
10	"	25.5	33.7	22.9	0.32	4	2.44	546

（a）ASTM882,所有试样正塑成5-10密耳薄膜，除了实例13和14，应变率均为1.0英寸/英寸·分，D,L-丙交酯是外消旋的。

续　　　表　　3：　增塑PLA(a)组合物的冠伸性能比较

实例号	组合物	丙交酯 %, TGA	弹性模量 1000 psi	1%割线模量 1000 psi	屈服强度 1000 psi	流动性 极限 %	破裂强度 1000 psi	破裂时延度 %
11	LDPE(b)	--	41.3	40.6	1.51	17	1.60	365
12	LLDPE(c)	--	44.4	42.7	1.66	16	1.66	599
13	双轴取向PE (d)	--	38.9	41.1	1.69	16	4.78	838
14	"(e)	--	35.6	38.5	1.68	16	5.20	940
15	HDPE(f)	--	127.8	120.9	3.48	9	1.95	216
16	PP(g)	--	174	174	5.08	5	7.34	6

(b) USI 低密度聚乙烯()聚乙烯213)。

(c) Exxon 线型低密度聚乙烯(LLPE6202,57)。

(d) 轴向。

(e) 交叉轴向。

(f) 菲利普高密度聚乙烯(HMN5060)。

(g) Clisso聚丙烯(XF1932, 熔融指数为0.52)。

表 4: 加工数据

原料	商标或试等级	密度 gm/cu cm	涂布的熔融温度 F	屈服 拉伸强度	弯曲 弹性模量 35 psi	熔融指数 gm/10 min
LDPE (USI)	聚乙烯 No. 213	0.924	360-550	1820	0.37	8.0
LLDPE (Exxon)	6202.57	0.926	425	1700	0.53	12.0
HDPE (Phillips)	HMN 5060	0.950	425-525	3600	1.75	6.0
80% LLDPE (Exxon) 20% HDPE (处理用油)	LPX 86 (Octene base)	0.927	260	--		0.8
聚丙烯 (PP-Chisso)	XF1932	0.91	450-500	5872	3.05	0.52
聚苯乙烯 (Amoco)	RI	1.05	400	7900	4.50	1.8

表3 给出了丙交酯和聚丙交酯混合物的某些数据。结果与用其它方法制备的实例1 和2 的类似组合物没有明显的不同。但是，本技术领域技术人员应当认识到物理性能有些细微的变化，这取决于混合物的紧密性、拉伸试验条件和制备该薄膜的加工技术。从表3 的对比情况表明丙交酯- 聚合物混合物的组分可控制在很宽的范围内，它们与许多通用非降解型塑料相似。

实例17：

低聚聚乳酸(OPLA)是按如下方法混合聚丙交酯而制备。将L-乳酸(956克) 的88% 溶液加入到带有机械搅拌器和瓶内温度计的三颈烧瓶(1升) 中。将反应混合物在通氮下于 150-190℃温度和200mmHg 压力下浓缩 1小时，直到稀释的理论水除去。除了乳酸和其低聚物外，不用催化剂。保持此温度和真空，并连续蒸馏 2小时直到除去脱水作用的73% 理论水。

所需的总时间是 3小时。在这时反应停止。将水样和瓶内低聚物用0.5N NaOH 滴定。在馏出水液中有26.2克乳酸。将瓶内低聚物 (OPLA) 与过量0.5N NaOH 回流，然后用标准硫酸再滴定。数据列于表5 。当热时，OPLA流动性质好，并有些冷流。聚合度为3.4 。与实例19的聚合物熔融共混后，用于实例20。

表5　　　实例1 OPLA的性能：

理论脱水量 %	滴定的酸 %	滴定的酯 %	表示成乳酸的总量 %	聚合度
58	34.4	82.4	116.8	3.4

实例18

重复实例17的方法，不同之处是更慢地进行蒸馏。加热 8小时，在此期间在200 mmHg压力下将温度由63℃慢慢升至 175℃，滴定瓶内试样以证明除去了理论水的62.2% 。滴定说明聚合度为4.3 。通过在 179℃

温度下加热和使用真空泵计 2小时，使OPLA的分子量进一步提高。OPLA不能在0.1N NaOH 中溶解，它是白色水液并且可以冷流。这种材料是具有比起实例1 更高聚合度的OPLA制备方法的第二种实例。在实例22和25中，它与聚丙交酯混合。经测定，聚合度约为6-10。

实例19

按照与实例3 相似的方法制备丙交酯的聚合物。90/10 重量比的L-/ 外消旋D.L-丙交酯共聚物进行熔融聚合，用0.02份（每百份）无水辛酸亚锡为催化剂。用相似的方法，制得100% L- 丙交酯均聚物(L-PLA) 。以90/10(重量）的共聚物/ 均聚物比在双螺杆挤出机中于 350°F 温度下将上述共聚物与均聚物熔融共混。用凝胶渗透色谱法测得共混物的重均分子量(Mw)为182,000，数均分子量(Mn)为83,000。用热重分析(TGA)，残留的丙交酯单体为1.7%（重量）。这种共混物与实例17的低聚聚乳酸(OPLA)混合可得到实例20的化合物。拉伸性能列于表6 。

实例20

实例19的聚合物与实例17的OPLA在一个敞开式两辊研磨机上于 325°F 温度下熔融共混20分钟。该混合物压塑成薄膜并如表6 所示测定。凝胶渗透色谱法分子量是光滑、单峰分布，Mw/Mn 为2.6,Mw为192,000，而Mn为73,000。

表 6: 90/10 聚丙交酯和低聚乳酸的熔融共混物的性能

实例号	组合物 %（重量）		丙交酯 %, TGA	弹性模量 1000 psi (a)	断裂强度 psi (a)	断裂应变 % (a)	Tg, C (b)
	聚合物	低聚物					
19	100(c)	0	1.7	298	7500	3	55
20	91(c)	9(d)	1.8	275	6113	2	--
21	100(e)	0	1.6	308	7478	3	58
22	70(e)	30(f)	0.4	254	5052	3	42
23	60(e)	40(f)	0.0	202	3311	2	38
24	50(e)	50(f)	0.0	106	2334	25	35
25	40(e)	60(f)	0.0	36	1180	129	35

(a) ASTM882; 5-10 密耳, 压塑薄膜, 应变率为1.0in/in/min.

(b) 由差示扫描量热法测定玻璃转化温度.

(c) 90% 的90/10 L-/D,L- 丙交酯* 共聚物与10% 聚（L-丙交酯）的共混物, 实例19.

(d) 实例17的低聚PLA

(e) 80% 的90/10 L-/D,L- 丙交酯* 共聚物与20% 的聚（L-丙交酯）的共混物.

(f) 实例18的低聚PLA

* 外消旋

实例21-25 ：

将实例19的共聚物与20% 实例9 所述的L-PLA 熔融共混。该共混物是列于表6 的实例21，它的分析数据和拉伸性能也列在表中。将实例21的聚合物依次与各种用量的实例18的OPLA熔融共混，如前述表6 所列测定实例22-25 。表7 列出了这些化合物的GPC 分子量。抗张强度和模量与图3 和图4 中的OPLA%(重量) (较低的曲线) 相比较。

表7：90/10 聚丙交酯和低聚聚乳酸的分子量和玻璃化转变温度

实例号	组合物%(重量)		残留单体 %(a)	GPC x 10⁻³(b)			M_w/M_n	Tg,(c) °C
	共聚物	低聚物		M_n	M_w	M_z		
21	100(d)	0	1.6	76	175	410	2.3	58
22	70(e)	30(f)	0.4	67(g)	136	299	2.0	42
23	60(e)	40(f)	0.0	61(g)	112	211	1.8	38
24	50(e)	50(f)	0.0	62(g)	114	223	1.8	35
25	40(e)	60(f)	0.0	69(g)	120	207	1.7	35

(a) 由TGA 测定残留单体。

(b) 由GPC 测定分子量。

(c) 由DSC 测定玻璃化转变温度。

(d) 90% 的90/10 L-/D,L- 丙交酯共聚物与10% L-Pla 的共混物

(e) 实例21

(f) 实例18

(g) 共混后，在 325°F 温度下用滚压式密炼混熔混共混。

所有D,L-丙交酯均为外消旋体。

实例26-30

将第二系列共聚物与OPLA共混。用与实例19和21相似的方法制备
92.5/7.5 L-/D,L-丙交酯共聚物。这就是表8 和9 的实例26。将其与实
例18的OPLA在一敞开式、双辊磨机中、 325°F 温度下共混大约20分钟。
将共混物压塑成 3-5密耳厚薄膜，并测定它们的拉伸性能和GPC 分子量。
各种性能记录在表8 和9 ，绘制在图3 和4 中。可看出虽然第二系列共
混物的分子量较低，但是它们的拉伸性能值明显地高。这是因为在高聚
合物组合物中残留的丙交酯单体和/ 或变化较少。所有的OPLA聚丙交酯
共混物可容易地压塑成不粘手的透明薄膜。

表 9 ：92.5/7.5 L-/外消旋D,L-丙交酯共聚物的分子量

实例号	% OPLA	GPC x 10^{-3}(a) M_n	M_w	M_z	M_w/M_n
26	0	63	124	228	1.95
27	20	60	108	189	1.81
28	30	48	80	125	1.66
29	40	59	96	151	1.65
30	50	56	92	141	1.64

(a) GPC

表 8．　92.5/7.5 聚合物组合和低聚物混合物的释放率和二元调制

序号 (d)	组合物 %(重量)		药剂量	释放率	释放速度	断裂应变	
	聚合物 (c)	低聚物 (d)	% TGA	(a)	(a)	% (a)	Tg(b) C
26	100	0	18.2	330	10,527	4	61
27	80	20	0.3	346	9,144	4	52
28	70	30	0.2	345	5,675	2	46
29	60	40	0.6	249	5,637	3	36
30	50	50	1.5	112	1,984	119	36

(a) ASTM882：3～5密耳压延薄膜；释放率单位：μg/in²/day。

(b) 差示扫描量热法测定玻璃转化温度。

(c) 92.5/7.5 L-丙交酯,L-丙交酯共聚物。

(d) 实例18

所有D,L-丙交酯是外消旋

实例31和32：

含有或不含增塑剂的薄膜试样在三月份至五月份暴露在Daytona，Florida 的海水中。水的pH值为7.3-7.6，含盐量为33.2-38.4ppt。在试验中，将水从15℃－27℃逐渐暖热。试样切成条样，放在海水中之前、之后和一定时间间隔测定拉伸性能。结果列于表10。所有试样显示了增白并物理降解，随时间递增。没有增塑剂的试样在海水中 6周后增白并降解。OPLA丙交酯共混物很快降解、 3周后就有显著的降解。加有20%丙交酯的化合物立即增白并在暴露 1周后就明显降解。

表 10: 在海水中暴露后的物理性能

拉伸性能, 1000 psi[a]

实例号	组合物	海水暴露时间 周	弹性模量	1%割线模量	屈服强度	断裂强度	应变 % 屈服	应变 % 断裂
31	90/10 共聚物 5% L-PLA	0	305	292	--	7.6	--	4.7
		3[b]	315	301	--	7.1	--	3.1
		6[c]	317	317	--	7.3	--	3.0
		9[d]	228	230	--	6.2	--	3.0
		12[e]	355	343	--	3.9	--	1.0
26	90/10 共聚物 10%低聚物	0	275	275	--	6.1	--	2.0
		3[b]	291	281	--	6.8	--	2.9
		6[c]	246	246	--	3.9	--	2.0
		9[d]	211	105	2.2	1.4	3	2.0
		12[e]	103	103	--	1.7	--	1.0
32	90/10 共聚物 1%富马酸	0	300	298	--	7.0	--	3.0
		3[b]	292	291	--	6.5	--	2.5
		6[c]	318	318	--	6.9	--	2.0
		9[d]	226	223	--	6.1	--	3.0
		12[e]	70	122	--	0.8	--	1.0
9	92.5/7.5 共聚物 20%丙交酯	1[e]	太脆无法测定					

(a)0.5×5in 薄膜条, 12-17 密耳; 应变率: 1in/in/min

(b)15-21℃ 咸海水 定期换水

(c)20-22℃ 咸海水 定期换水

(d)22-23℃ 咸海水 定期换水

(e)22-27℃ 咸海水 定期换水

上述实例证实所有乳酸组合物是柔韧的热塑性塑料，并用于柔性塑料容器。为了比较，非增塑的均聚（L-丙交酯）是高结晶度聚合物，它们拉伸强度约为7000psi，延伸率为1%，起始模量为500,000psi。它是非常脆的，不透明的并很容易裂开。它不具有热塑性，也不透明。聚（外消旋D.L-丙交酯）是非结晶的玻璃态聚合物。该聚合物的玻璃化转变温度约为50℃，拉伸强度约为6300psi，伸长率约为12%，起始模量为169,000psi。它虽然透明，但也非常脆。完全相反，用丙交酯单体增塑的L-丙交酯/外消旋D.L-丙交酯共聚物的聚合物完全不同。例如，增塑的聚合物的拉伸强度约为3900psi，伸长率为431%，起始模量为56,000psi。增塑的聚合物是透明和无色的。共混物必须加热至100℃以上才可除去增塑剂。

虽然，理论上预计增塑的结果是有更多的非结晶结构，但是令人惊奇的是生成了铼性、透明、稳定的组合物，以及其性能类似于聚乙烯，正适于某些包装应用的需要。由于可在环境中生物降解的材料可以缓解塑料污染问题，所以希望这种材料能同时具备上述初始性能，本发明正是满足了这种需要。

本技术领域专业人员可知当聚物和增塑剂极为紧密相容的共混物是少见的。增塑作用使初始物理性能和环境生物解降时间可在很大范围内变动。

聚合物中增塑剂的置取决于所需组合物的特性。如果丙交酯用作为增塑剂，用量较好为5-40%（重量），而如果仅用丙交酯或乳酸低聚物则用量为2-60%（重量）。令人意外地发现，低聚物加入多达30%（重量）时基本上不影响拉伸强度或模量。参见图3和4。加入30-60%（重量）低聚物可产生明显的增塑作用并减弱了物理性能。向组合物中加入低聚乳酸是非常经济的，因为它比乳酸高聚物便宜。低聚物是由乳酸或任何丙交酯制备。要注意很自要的是乳酸低聚物通常含有大量的乳酸，除非将

其除去。这是制备具有特定性能的组合物时重要的考虑因素。本技术领域的技术人员和了解本发明技术的人员可选择反应条件以制得适当链长的聚合物、选择聚合物和增塑剂比例，以便得到具有与通常所用包装热塑性塑料相类物理性能并且相对讲较快降解的可二次加工组合物。例如，较高用量的增塑剂使得聚合物的柔性和韧性等物理性能提高，但是，它的降解速度也提高了。另外，短链聚合物需要较少的增塑剂，便可得到与长链聚合物相同的性能。

本发明第一实施方案的另一方面是提供了制备环境生物降解组合物的方法，该组合物是的式（I）乳酸的增塑聚合物。该方法包括制备一种或多种丙交酯单体和催化剂，聚合该单体，以形成聚合物，聚合温度要足够低以便在完全聚合之前使聚合反应停止；测定单体的量以确定所剩单体的量；在聚合反应完成之前，在达到预定单体含量时停止反应，从而该确定量的未反应单体截留在聚合物中。本方法的丙交酯单体是选自D-丙交酯、L-丙交酯、内消旋D,L-丙交酯、外消旋D,L-丙交酯及其混合物。可任意地把附加增塑剂加入到聚合物中，增塑剂还选自L-丙交酯、D-丙交酯、外消旋D,L-丙交酯、内消旋D,L-丙交酯、乳酸、乳酸低聚物、丙交酯低聚物及其混合物。单体聚合最好是在低于 129℃温度进行。另外将增塑聚合物制成最终产物时，最好是在足够低温度下进行，使增塑剂能保留在聚合物中。这个温度大约为 129℃。如果加入了附加的单体和/或低聚物，当然单体的保留就不那么重要了。

本发明第一实施方案还提供了一种制备式I化合物的方法，该方法包括制备一种或多种丙交酯单体和催化剂，聚合单体形成聚合物，用另一步骤将增塑剂加入到聚合物中，该增塑剂选自D-丙交酯、L-丙交酯、D,L-丙交酯、乳酸的低聚物及其混合物。

本发明的组合物具有拉伸强度为300-20,000psi，断裂伸长率为50-1000%，正切模量为20,000-250,000psi。作为较好的聚烯烃替代物，

本组合物的拉伸强度至少为3000psi,断裂伸长率至少为250%,正切模量至少为50,000psi。

本发明的均聚物和共聚物是不溶于水的,但持续与水接触是要慢慢地降解的。但是,相比起本发明聚合物所代替的聚烯烃组合物,降解作用是较快的。因而,由本聚合物制备的物质扔掉后,在环境中慢慢地降解成为无害的物质。如果将由本发明组合物制备的物质焚烧,它们发出纯净的蓝色火焰。

本发明的第一实施方案的另一方面是提供了用本发明生物降解组合物替代热塑性组合物的方法,其中热塑性组合物包括第一种可取向的聚合物单元,该方法是用第二种可取向的聚合物替代第一种可取向聚合物单元,第二种可取向的聚合物非取向接伸强度为300-20,000psi,断裂伸长率为50-10,000%正切模量为20,000-250,000。其中第二种聚合物包括式（I）结构的聚乳酸单元,其中n为重复单元数,为整数,且150<n<20,000,第二种聚合物是用增塑剂增塑的,增塑剂选自丙交酯,乳酸低聚物、丙交酯低聚物及其混合物。该方法可用于聚烯烃组合物,特别是聚乙烯和聚丙烯,以及聚氯乙烯和聚对苯二甲酸乙二醇酯。除了上述所列,该方法还适用于替代苯乙烯、乙酸乙烯酯、甲基丙烯酸烷基酯、丙烯酸烷基酯的聚合物。应该理解由所列单体的混合物制得的共聚物和上述共聚物与聚合物的机械混合物也是可置换的。

第二通用实施方案:

作为第二实施方案在环境中生物降解组合物是完全降解成环境可接受的相容物。降解的中间产物是乳酸,它可自然地广泛分布在发生物上,该物可由多种生物体很快代谢。它的天然降解最终产物是二氧化碳和水。这些组合物的预期等同物如含有少量其它物质、填料或扩充剂的组合物也是可以通过适当选择物质来使它完全环境降解的。本组合物是环境可接受的物质,因为它们的物理劣化和降解作用比起被它们取代的常用非

降解塑料更快并且完全。此外，因为所有组合物或组合物的主要部分是聚乳酸、和/或聚乳酸生成的丙交酯或低聚物，没有残留物或仅有少部分较慢降解的残余物留下。这种残留物的表面积大于本体产物的表面积，并且有较快的降解速率。

本发明的较好组合物包括具有式（Ⅰ）重复单元的聚合乳酸单元，其中n是75-10,000的整数，α-碳原子是D和L（或R和S)无规混合物并有一种纯对映体偏多。当n较小时，聚乳酸PLA是容易加工的，但是认为它比n为较大时软弱，当n很大时，如7000或更大，PLA是非常强韧，但是难以注塑成型。较好的n大约为500-3000，可得到熔融加工性和最终使用物理性能的最好综合。单体选自L-（或D)/D,L-比例的聚合乳酸或它们的环化二聚物、丙交酯，这在以后讨论。乳酸和丙交酯都可提供PLA重复单元，如上所述。但是丙交酯较好，因为它更容易得到较好物理性能所需的高分子量。因为丙交酯的结构为：

$$
\begin{array}{c}
CH_3 \\
O-C-H \\
O=C \quad\quad C=O \\
H-C-O \\
CH_3
\end{array}
$$
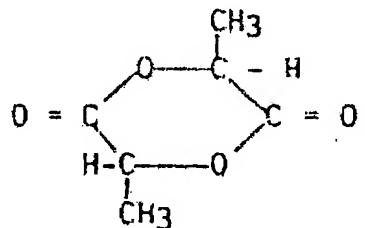
它有二个对称α-碳原子，所以有三种类型丙交酯，即D,D-（或D-)，L,L-（或L-)，和内消旋D,L-丙交酯。

D-丙交酯是D-乳酸的二丙交酯或环化二聚合物。类似地，L-丙交酯是L-乳酸的环化二聚合物。内消旋D,L-丙交酯是D-和L-乳酸的环化二聚物。外消旋D,L-丙交酯包括D-和L-丙交酯的50/50混合物。当在此单独使用时，术语"D,L-丙交酯"是指包括内消旋D,L-丙交酯或外消旋D,L-丙交酯。在此所用术语"分散的"是指物质是均匀的或完全地与聚合物混合。

纯L-PLA的加工特性很差，容易裂开和变得不透明。纯D,L-PLA容

易加工，但是没有足够的刚性来满足OPS 补偿。本发明较好的实施方案是共聚物中L-丙交酯／D,L-丙交酯比例为85/15-95/5，最好为90/10。当比例大于95/5时，共聚物热成型极易破裂，并在室温下容易变得不透明。当比例低于85/15 时，丙交酯共聚物具有低于OPS 补偿所需的模量。在这两个极限之间的共聚物在一般的塑料技术的制备／加工设备中，熔融下淬火，得到透明、无色和特别刚性的薄膜和模制品。按上述制成的制品性能是与OPS 的性能非常相近似。

本发明的另一个优点是所有乳酸共聚物可利用便宜的原料。由淀粉和玉米得到的玉米糖浆可发酵成L-或外消旋D,L-乳酸，这取决于微生物。外消旋D,L-乳酸可由乙烯经济地得到，即，将乙烯氧化成乙醛，再与氢化氰反应形成乳腈，该乳腈水解成外消旋D,L-乳酸。将乳酸蒸馏容易地得到丙交酯。用普通蒸馏／缩合方法将乳酸转化为丙交酯，不对称碳原子的立体化学结构是没有变化的。

当在此讨论L-丙交酯和D,L-丙交酯反应时，应当理解对L-丙交酯特定的反应也可用于D-丙交酯。因而，按照在此叙述的方法，D-丙交酯和D,L-丙交酯反应得到等同的产物，仅仅不同的是在不同方向的旋光性。

本发明的共聚物较好的制备是，加热单体的混合物形成均匀熔融体，加入催化剂使丙交酯进行开环聚合反应，聚合反应较好的是在惰性、无水气氛如氮气或氩气中，大气压或真空下进行。适宜的催化剂包括二价金属氧化物和有机金属化合物如辛酸亚锡、乙酸锌、乙酸镉、乙酸铝或丁酸铝、氯化钛、苯甲酸钛和氧化镉。辛酸亚锡是较好的催化剂，因为它在单体中较高的溶解性，容易制成无水形式，并且低毒。所需催化剂用量为基于单体的约0.02-2%(重量)，较优选的是约0.2%。共聚物的分子量和熔融粘度是由催化剂和／或链转段剂如乙醇酸的用量来控制的。聚合反应的温度约为 100-200℃。最小色彩形成要在 140℃ 以下，而聚合速度在 135℃ 温度以上最好。因为在 127℃ 温度下外消旋D,L-丙交酯

熔融，最好在127℃温度以上进行单体转化为聚合物的聚合反应。

作为与OPS补偿需要纯净和透明时，本发明共聚物是在惰性气氛中，在它们的熔点上，一般为125~150℃下聚合。熔融丙交酯共聚物由聚合器以编织原料状和棒状挤出、淬火、制成颗粒并贮存在袋中、以便以后用于模塑和挤压成型中。

相似地，透明的热成型包装膜和成型品是这样制备的，在共聚物熔点以上温度模塑和挤出，并快速冷却此加工品。因而，共聚物仍是透明的，除非在玻璃化转变温度Tg以上和熔点Tm以下加热几小时，热成型片材、厚块、薄膜和模塑品的慢慢冷却可在共聚物中产生球状微结晶，这改善了加工品的热稳定性，且使得透明度有些下降。使用成核剂如苯甲酸钠、乳酸钙等等也可加速和加大结晶。在Tg和Tm之间，适当拉伸共聚物可造成聚合物分子取向，并且可基本上改善物理性能而透明性不下降。

不同类型的丙交酯聚合物或共聚物共混可基本改变其物理性能。例如，高熔点L-丙交酯聚合物与低熔点丙交酯共聚物的熔融共混可得到具有足够量和类型的结晶来保持透明度的一种透明材料。本技术领域技术人员应认识到模制薄膜的透明性、较大刚度、较高的热变形温度、较好热加工性和环境生物降解性，这是较少有的好综合性能。因而，聚合物可共混，以及成核、取向和用分子量来控制，以得到最终化合的热塑性塑料的加工性和最终性能在很大范围变化。

本发明的共聚物在水份下水解回到乳酸。在空气中和潮湿下，12个月-18个月时间明显水解，共聚物变得粘稠、有些不透明并非常脆。当浸入水中，共聚物用1-4个月时间就水解了。时间长短决于组合物、分子量、室温、表面与体积比，特别是共聚物所处环境的含水量。微生物可使乳酸成为二氧化碳和水。大致测定，共聚物的贮存期为几个月，在非常潮湿下的1年内就消失了。

下列的实例进一步说明本发明。实例1B至7B是制备和评定组合物类。

可发现，与先有技术相反，L-丙交酯/ D,L-丙交酯共聚物的加工性能和物理性能是完全不同与先有技术的。

实例1B：

在 500毫升圆底干燥烧瓶中装入 160克L-丙交酯(Purac公司制造，"三星"级）和40克外消旋D,L-丙交酯(Purac公司制造，"三星"级）。该混合物在 123-129℃温度下加热大约 1小时，同时通过塞子的入口和出口连续地吹入氮气。单体成为透明熔融体，摇动该熔融体来充分混合。制备催化剂溶液并共沸蒸馏干燥，也就是，将10毫升辛酸亚锡(Polysciences 公司制造）溶解在60毫升甲苯中，将含有痕量水的10毫升甲苯蒸馏到迪安－斯达克榻分水器中，然后通过一个干燥管排出。将0.20毫升辛酸亚锡溶液吸移到熔融物中，并充分混合。连续吹入氮气。熔融物的粘度在以后 3小时内增加了。在 123-127℃温度下连续加热 20-24小时。将混合物放置冷却至室温，在保护罩下放入液氮来进一步冷却烧瓶。玻璃瓶破碎并用液体从聚合物中除去碎玻璃。共聚物是无色和透明的，并且进行了一系列试验，列于表1B。在 170℃温度下用热液压法压塑薄膜，用于拉伸试验。模制成 1/8英寸厚的厚块用于冲击试验（缺口悬臂梁式冲击试验，ASTM，D256）和热变形温度(ASTM，D648)测定。用差示扫描量热法(DSC）测定玻璃化转化温度(Tg)和熔点(Tm,吸热线的中心）。

实例2B-7B

重复实例1B的方法，不同之处是L-和外消旋D,L-丙交酯的比例按表1B所示变化，试验结果列于表1B。实例7B的纯L-丙交酯聚合物在170－200 ℃温度下总不能模塑好，因为模塑冷却时，它总是严重破碎。通常，冷却了，它就不透明。

表 18: L-丙交酯 / 外消旋 D,L-丙交酯共聚物的性能

组合物中L-丙交酯/D,L-丙交酯(外消旋)的重量比	80/20	85/15	87.5/12.5	90/10	90/10	95/5	100/0
实例号	18	25	30	48	58	68	78
颜色/透明度	无色透明	←					白色不透明
膜厚密耳	10	5	15	11	5	10	5
拉伸强度 1000 psi, ASTM D882	7.9	6.9	3.3	8.5	8.2	9.2	(a)
伸长率 %	3.5	5.8	6.0	7.1	7.2	5.1	(a)
正切模量 1000 psi	289	221	694	210	258	746	(a)
缺口冲击强度 ft-lb/in.	(b)	0.44	0.34	0.31	--	0.41	(a)
M_w, 1000's	--	928	--	--	--	--	--
M_n, 1000's	--	218	--	--	--	--	--
T_g, C(c)	53	53	48	44	--	46	--
T_m, C(c)	--	--	125	133	--	152	190

(a) 冷却时破碎，太脆不能试验

(b) 缺口试样，1/8英寸厚试样，在缺口处冲击。

(c) 用10℃/分的加热速率和氮气下进行差示扫描量热法。

实例8B：

与实例4B和5B相似，制备L-丙交酯/外消旋D,L-丙交酯的重量比为90/10的共聚物。用氮气吹扫的2升干燥烧瓶中加入1045.8克L-丙交酯和116.4克外消旋D,L-丙交酯。加入1.0毫升无水辛酸亚锡溶液（每毫升甲苯为0.2毫升）。该烧瓶用氮气吹扫过夜，然后在141℃油浴中加热至到单体熔融并充分混合。慢慢地降低加热温度至125℃并连续72小时。聚合物冷却时慢慢地变白。除去玻璃后，得到混浊的、无色、玻璃态共聚物。凝胶渗透色谱法测定重均分子量(Mw)为532,000,数均分子量(Mn)为149,000。

丙交酯聚合物的DSC表明Tm确为145℃，参见图10。将丙交酯聚合物熔融、淬火和用DSC再测试，结果说明没有结晶度或熔点。但是，Tg约为50-55℃。结果表明该聚合物是结晶的或非晶形，这取决于它的热过程。

实例9B-12B：

用实例1B的方法制备组合物系列，不同之处是使用其它L-和外消旋D,L-丙交酯的比例、在125℃温度下加热2小时，125-147℃温度下加热14小时，147-131℃温度下加热2小时。结果列于表2B。

表2B：　　L-丙交酯和D,L-丙交酯共聚物的拉伸和模量性能

组合物				
L-丙交酯与D,L-丙交酯（外消旋）的重量比	70/30	60/40	20/80	0/100
实例号	9B	10B	11B	12B
颜色/透明度	无色/透明			
膜厚，密耳	6~9	4-6	4-5	2~7
拉伸强度				
1000psi ASTM D638 (1)	6.9	6.7	5.8	5.6

性能			
伸长率%	3.2	3.0	2.7	2.8
正切模量　1000psi	287	293	275	278

(a) 薄膜以0.2″/min的夹口分开速度拉伸，记录纸速为5″/min。

上述实例的结果说明只有某些组合物具有OPS补偿所需的性能。对OPS类物质所需的主要性能是透明和无色、拉伸强度大于7000psi，正切模量（刚度的测量）大于400,000psi和较好的热塑性。表3B列出了结晶聚苯乙烯（OPS）与87.5%（重量）L-丙交酯和12.5%（重量）外消旋D,L-丙交酯无规共聚物的某些逐项对比。

表3B: 物理性能比较

性能	聚乳酸 实例3B	结晶聚苯乙烯
缺口冲击强度英尺-磅/英寸	0.4	0.4
极限拉伸强度　psi	8300	7400
伸长率%	6.0	4.0
弹性模量　psi	694,000	450,000
变形温度 °F（在264psi载荷下）	(a)	200
比重	1.25	1.05
洛氏硬度	(b)	M75
维卡软化点，°F	(c)	225
熔体流动速率	40-46(d)	1.7克/10分(e)
D1238(G)		1.6克/10分(f)

(a) 取决于热过程。

(b) 肖氏D-97。

(c) DSC，在10℃/分下 T_m~125℃（257°F）。

(d) 在较低温度下流动速度下降。

(e) 按制备方法所列。

(f) 本实验。

实例13B

将实例2B的共聚物模塑，并反复模塑几次以确定是否在薄膜上出现颜色，并保留高的分子量。这确定了共聚物是否可循环加工，这是实施加工方案的重要参数。表4B的结果表明，共聚物在反复加热和模塑后，尽管共聚物在较高的温度下反复暴露在空气中，仍然是完全透明和无色的。

表4B：　丙交酯共聚物模塑情况

实例号	过程	外观	Mw×1000	Mn×1000	Mw/Mn
实例2B(a)	没有模塑 直接聚合	完全透明 和无色	928	218	--
实例13B(a)	实例2B共聚物 模塑后 (b)	--	301	13.5	2.22
实例13B(a)	实例2B共聚物 模塑 6次后 (b)		137	56.7	2.42

（a）85/15,L-丙交酯/外消旋D,L-丙交酯共聚物。

（b）在167℃(333°F)温度下压塑7分钟成为5-密耳薄膜。

实例14B-18B：

实例2B、3B和6B的共聚物压塑成为大约20~30密耳厚的薄膜，并放入加热的Instron试验机中，将该薄膜以0.5英寸/分的速度和83℃温度下拉伸至它的长度的5倍。该薄膜从Instron试验机中取出后，快速冷却，得到大约5密耳厚的薄膜。这些薄膜为透明和无色的。测定拉伸性能并列于表5B。当拉伸至它们长度的8-10倍时，薄膜出现光雾并有些不透明，说明形成了结晶。

所得结果说明，制得的非常薄的薄膜具有合适的对OPS补偿的硬度和透明性。因而，尽管丙交酯共聚物的密度相比起聚苯乙烯较高，但基本上没有其它材料可对OPS硬度补偿

表5B:　　　取向(a)后L-丙交酯/外消旋D,L-丙交酯共聚物的性能

组合物					
L-丙交酯/ D,L-丙交酯（外消旋）的重量比	85/15	85/15	85/15	87.5/12.5	95/5
实例号	14B	15B	16B	17B	18B
膜厚　密耳	5 5	5.0	6.5	5.0	4.0
拉伸强度　1000psi	14.0	14.7	15.0	13.0	16.0
伸长率,%	31.5	15.4	30.0	23.8	37.4
正切模量　1000psi	--	564	419	432	513

(a) 在Instron 机上、以0.5in/min 拉伸速率、在83℃温度下5X取向。

实例19B：

将表1B的丙交酯共聚物薄膜浸入水中几个月时间。大约2个月,共聚物还是透明的,3个月后出现一点光雾,放在潮湿空气中架子上并多次处理后,薄膜实际上约1年时间仍没有变化。虽然几个月后,强度和伸长率的Instron 试验数据有缓慢地下降。在废碴埋填中,放入的薄膜在6个月-2年消失,时间长短取决于废碴埋填的湿度、pH、温度、组合物、表面-体积比,以及生物活性。所有薄膜的燃烧是纯净的兰色火焰。

实例20B：

实例5B的丙交酯共聚物（淬火、压塑薄膜）用DSC 测定,得知在邻近130℃温度下,结晶度小于2%,参见图5。实例5B共聚物的1/8英寸厚试样在185°F 烘箱中退火16小时。试样变得光雾,并且试样的DSC表明（参见图7)结晶度显著提高。该试样在264psi下的热变形温度(HDT)为90～95℃。没有退火的相似试样具有的热变形温度为50～55℃,与它的Tg值相同。

实例21B

5%（重量）乳酸钙与实例5B丙交酯共聚物在热辊磨机中,170℃温度

下，共混大约5分钟。共混物以片状从辊中拉出，并测试。它是硬的、强韧并光雾的。在82倍光学显微镜下测出非均匀区域，区域大小为几微米～30微米。DSC 表明在约 145℃温度下，结晶度基本上增大了（参见图8），仍然可淬火和反复加热。上述结果与实例8B、20B 和21B 比较表明，成核剂可较好有效的在丙交酯类聚物中产生结晶。可使用的成核剂如羧酸的盐，较好的是乳酸的盐。

实例22B

在装有机械搅拌器和氮气入口和出口的500 毫升，三颈圆底烧瓶中，装入180.7 克L-丙交酯和40.2克外消旋D-、L-丙交酯（都是Boehringer 和 Ingelheim 制造S 级）。在氮气吹扫下，将烧瓶的内含物加热至 110℃ 以熔融丙交酯。加入20.1克聚苯乙烯(Amoco，R3，熔融指数为3.5 克/10分）。聚苯乙烯较大的溶胀，并预先加热至 185℃温度下搅拌过夜而部分溶解。将温度降至 141℃，加入0.2 毫升无水辛酸亚锡溶液(0.2毫升/ 毫升甲苯）。停止搅拌，在3 天时间 141℃温度下让丙交酯聚合。停止搅拌后，大溶胀的聚苯乙烯浮在上部。冷却低部的聚丙交酯相，用DSC 测试。试样具有较低的Tg，大约35℃，另一方面它缺乏表观温度转化。压塑薄膜是透明、无色和非常柔韧的。这些结果表明，聚苯乙烯是完全断续的形成结晶。

实例23B

实例8B的丙交酯共聚物与20%（重量）实例7B制备的L-丙交酯均聚物磨辊共混。均聚物的试样用DSC 法分析，参见图11。共混的试样用DSC 法测定，得知Tg为59～63℃，Tm为 150和 166℃，参见图12。薄膜是透明的至有少量光雾，这取决于压塑后它们的冷却速率。淬火试样在加热至大约80～90℃时，容易结晶。结果，共混物的热变形温度非常高，在80～90℃温度下，共混物光雾了，但是没有象非共混的90/10 共聚物那样热变形。非取向压塑薄膜的拉伸性能列于表6B，并与聚苯乙烯类似所

得数据相比较。

表6B: 实例23B 聚丙交酯和结晶聚苯乙烯共混物的比较

	实例23B[a]	结晶聚苯乙烯[a,b]
膜厚：密耳	8	14
抗张强度 ASTMD882 ×1000 psi	7.7	6.0
伸长率% 至断裂	6.5	3.2
正切模量×1000 psi	323	267

（a）薄膜、非取向、压塑试样

（b）熔融指数：1.7

　　本实例说明，熔融共混是改善共聚物性能的优异方法，这样可得到与聚苯乙烯相似的优异性能。基于共混有聚合物的L-丙交酯（或D-丙交酯）的均聚物用量越大、热变形温度越高，但是混浊度也提高了。这种加入均聚物可与其它提高聚苯乙烯类性能的方法一起应用，而仍然保持透明度。

　　另一个实例是，由聚合物制备的取向薄膜可提高拉伸性能。以8-10倍地拉伸，物理性能仍然提高，但是材料变得光雾了。因而，取向度也需要控制，并与其它改进方法的性能合并考虑，以获得优异的聚苯乙烯类性能。

实例24B ～27B

　　实例24B ～27B 是丙交酯在有可控制量链转移剂下聚合，说明用链转移剂如乙醇酸可控制分子量，结果示于表7B。链转移剂用量与重均分子量的倒数间有近似的线性关系，较好的链转移剂是乳酸。

表7B: 用链转移剂控制分子量

实例号	PPH of(a) CTA	M_n(b)	M_w(b)	M_w/M_n
24B	0.22	13,500	107,300	8.0
25B	0.45	12,800	66,700	5.2
26B	0.90	7,300	29,900	4.1
27B	1.80	4,700	13,900	2.9

(a) 在聚合配方中，每100 份丙交酯的乙醇酸链转移剂 (CTA) 份数。

(b) 凝胶渗透色谱法，在四氢呋喃溶剂中，23℃温度下，用10^6、10^5、10^4 和 10^3 anhstrom柱。数均分子量Mn和重均分子量Mw比较单分散聚苯乙烯标准计算。

实例28B

将实例2B丙交酯共聚物的4 密耳厚压塑膜用ASTM法作为防护膜来测定。结果示于表8B。丙交酯共聚物对二氧化碳和氮的防护比聚苯乙烯好得多。相比起一些其它的聚合物防护膜，丙交酯共聚物是适用于许多包装应用的防护膜。

表8B: 实例8B对气体的渗透性(a)

气 体	丙交酯共聚物 实例2B	结晶聚 苯乙烯(b)	对苯二 酸酯	偏氯乙烯 一氯乙烯 共聚物(b)
立方厘米/100平方英寸/ 24小时/ 大气下				
CO_2	32.1	900	15~25	3.8~44
O_2	19.9	350	6~8	0.8~6.9

(a)ASTM D1434～75，实例2B是4.0 密耳厚压塑膜。

(b) 由现代塑料百科全书得数据。

实例29B

将1/8 英寸厚的片状实例1B～6B丙交酯共聚物浸入到石油醚和二氯甲烷的混合物中过夜，石油醚/ 二氯甲烷的比例为70/30 ～60/40,当放在沸水中，共聚物成为泡沫体。形成了充分发泡的不规则泡沫。

实例30B

将工业的结晶聚苯乙烯(201型,Huntsman Chemical公司出产) 和实例8B丙交酯聚合物的熔融粘度相比较。用标准的 5千克负荷和在 200℃温度下，聚苯乙烯的熔融指数(ASTM D1238(G)) 为1.6 克/10 分。在相同条件下，丙交酯聚合物的熔融指数为:40-46克/10 分，但是,160℃温度下为8.0 克/10 分。通过观察Instron 毛细管粘度计的两种聚合物的熔融粘度来更详细地比较熔融粘度。比较的结果示于图9 。在挤出和注射成型中通常受到的剪切率约为100-1000秒$^{-1}$。分析图9 的数据表明，

160℃温度下丙交酯聚合物的熔融粘度与 200℃温度下聚苯乙烯的熔融粘度非常相近。

上述结果说明，丙交酯聚合物可在温度低于聚苯乙烯加工温度的温度下，用非常相近的方法熔融加工。

实例31B-34B ：

纯化的（重结晶并干燥）内消旋丙交酯（内消旋D,L-丙交酯）进行少量的试验性聚合，成为均聚物和共聚物。用GPC 法测定分子量并与D,L-丙交酯的类似物比较。结果列于表9B。聚合物熔融压制成薄膜，测定它们的物理性能并比较，示于表10B 。用不同片厚和分子量进行试验，共聚物的试验性缺点是相似的。内消旋丙交酯的均聚物是较弱的。

表 10B：D,L-和内消旋丙交酯聚合物和共聚物的物理性能比较

实例号	聚合物组合物	弹性模量 100 psi	断裂拉伸强度 100 psi	断裂伸长率 %	膜厚 mil	应变率 in./min.
31B	D,L-丙交酯均聚物	278	5.6	2.8	5-7	0.25
32B	内消旋丙交酯均聚物	345	3.8	3.5	9	0.25
33B	90/10 L-/内消旋丙交酯共聚物	190	7.9	3.8	12-15	0.25
34B	90/10 L-/D,L-丙交酯共聚物	323	8.6	4.6	4-6	0.25

(a) 压塑薄膜

表 9B: 内消旋和外消旋丙交酯聚合物和共聚物的GPC 分子量比较

实例号	组合物	Res. Mon., %	GPC x 10^{-3}			
			M_n	M_w	M_z	M_w/M_n
31B	D,L-PLA	--	97.5	341	757	3.49
32B	内消旋 PLA	2.76	62.5	152	264	2.42
33B	90/10, L-/内消旋	1.67	29	142	301	1.67
34B	90/10, L-/D,L	--	91.3	201	350	2.20

本发明第二实施方案组合物的概述包括一种环境生物降解的聚合物，该聚合物包括式（Ⅰ）结构聚合乳酸单元，其中n 为75-10,000 的整数，α碳原子是L-和D-构型的混合物，并且或是D-单元偏多或是L-单元偏多，其中聚合物是聚苯乙烯的合适替代物。聚合物的D-和L-单元较好的是由85-95重量份L-丙交酯或D-丙交酯和15-5重量份D,L-丙交酯制备的。

更相似于聚苯乙烯的具有改进性能的在环境中生物降解组合物包括式（Ⅰ）结构的聚合乳酸单元（其中n 为75-10,000 的整数，α碳原子是L-和D-构型的无规混合物 并且或是D-单元偏多或是L-单元偏多，与D-丙交酯或L-丙交酯的丙交酯均聚物的共混物。n 为150-10,000整数的组合物具有较好的强度和熔融加工性的综合性能。

制备第二实施方案的组合物的方法综述包括将L-丙交酯或D-丙交酯单体和D,L-丙交酯单体与催化剂混合，加热并熔融，从而L-丙交酯单体或D-丙交酯单体的含量为 85-95重量份，D,L-丙交酯单体的含量为15-5重量份，而制成均匀溶液，聚合该溶液，处理该聚合物以改善其性能，从而制得适于替代聚苯乙烯的聚合物。组合物的性能可用如下方法调节，加入成核剂，共混加入D-丙交酯或L-丙交酯均聚物以制得一种机械混合物；聚合物取向；共混加入成核剂和D-丙交酯或L-丙交酯聚合物；共混加入成核剂和D-丙交酯或L-丙交酯聚合物并使聚合物取向，在聚合

步骤中加入链转移剂以调节它们性能成为聚苯乙烯替代物，在较高温度下退火，并加入附加的增塑剂，该增塑剂选自D-丙交酯、L-丙交酯、内消旋D,L-丙交酯、乳酸、丙交酯低聚物、乳酸低聚物及其混合物。如果一种单体选作为增塑剂，加入与组合物中所得聚丙交酯所用不同的立体化学结构的低聚物，可制得独特的产物。在惰性气氛中和反应温度较好为 140℃ 或低温度下进行聚合，不会制得有色物质。一旦了解本发明的技术，可使用上述处理的各种综合，制得本领域技术人员认为合适的优异性能。

正如上述第一实施方案所提到的，单体或低聚物的较高用量可有明显效果。在此处第二实施方案，单体和低聚物的较小用量可较好地获得硬度。增塑剂的用量为0.1-5%较好。组合物中通常含有增塑剂的用量取决于聚合条件或聚合后的加入量。作为增塑剂的附加单体选自D-丙交酯、L-丙交酯、内消旋D,L-丙交酯、外消旋D,L-丙交酯及其混合物。也可以加入丙交酯或乳酸的低聚物。加入立体化学结构不同于组合物中聚合物的单体或低聚物可制得独特组合物。

本发明第二实施方案还提供了用本发明的生物降解组合物替代热塑性组合物的方法，而热塑性组合物包括第一种取向聚苯乙烯单元，可用第二种取向的聚合物替代第一种取向聚合物，第二种取向聚合物非取向时具有拉伸强度至少为5,000 和正切模量至少为200,000，其中第二种取向聚合物包括式Ⅰ结构的聚乳酸单元，其中n 为重复单元数，n 是75<n≤10,000的整数，α碳原子是L-和D-构型的混合物，并且或者D-单元偏多或者L-单元偏多，其中聚合物是 85-95重量份L-或D-丙交酯以及15-5重量份D,L-丙交酯制备的，该聚合物可用0.1-5.0%（重量）增塑剂增塑，增塑剂选自丙交酯、乳酸的低聚物、丙交酯的低聚物及其混合物。

本发明组合物的预期等同物是含有少量其它物质的组合物。如果需要，可加入交联剂、其它增塑剂、着色剂、填料等等来改性本发明制备

62

的组合物。

在此的组合物可熔融加工成具有自撑结构的有用制品，如一次应用容器、餐具、盘子、板、饮料杯、份饭盘、注射器、医用盘、包装膜等等。该组合物具有通常聚苯乙烯的特性并可替代聚苯乙烯，还可环境降解。该组合物特别适用于一次性使用的制品，或在丢掉前短时间使用的制品。

第三通用实施方案：

第三实施方案公开了聚乳酸（PLA）与聚苯乙烯（PS）、聚乙烯（PE）、聚对苯二甲酸乙二醇酯（PET）和聚丙烯（PP）的共混。本实施方案公开了聚乳酸与常用热塑性塑料熔融相容，以及对它们物理性能的效用。

在此公开的在环境中降解组合物是至少部分降解。组合物的聚乳酸部分比起共混物的稳定部分可相当快速地分解，并造成共混物的物理性能劣化。例如，当组合物是紧密的，并与小粒度均匀共混，其物理性能的劣化破坏了原有产物。在此组合物提供了环境可接受的材料，因为它们的物理劣化和降解比起常用非降解塑料要快得多。另外，因为此组合物的绝大部分是聚乳酸和/或乳酸生成的丙交酯或低聚物，仅留有少量非常慢降解的热塑性塑料（如聚苯乙烯），这种残留物具有较大的表面积并希望比本体状产物分解快得多。

D-丙交酯是D-乳酸二元内酯或环状二聚物。类似地，L-丙交酯是L-乳酸的环状二聚物。内消旋D-.L-丙交酯是D-和L-乳酸的环状二聚物。外消旋D,L-丙交酯包括D-和L-丙交酯的50/50混合物。当在此单独使用时，术语"D.L-丙交酯"是指包括内消旋D,L-丙交酯或外消旋D,L-丙交酯。聚乳酸可由上述一种或多种丙交酯制备。

实例1C：

聚苯乙烯与聚乳酸溶剂共混并且用二氯乙烷溶剂浇铸，以确定最佳的相容性。溶剂浇铸薄膜是半透明的，并且外表不象干乳酪。试样外表

看起来是均匀的，并且耐折和耐摆弄而不会破碎。在310倍的光学显微镜下观察，显示出有3微米或更小的非均匀区。该共混物具有非常好的相容性。二年多，试样没有短效材料的"白化"现象，也没有证明其降解的物理性能变化。

实例2C：

聚丙烯8525（Hercules）与聚乳酸在Brabender机中400°F下熔融共混。所制PP/PLA的比例为100/0（对照组），90/10和75/25。

实例3C-5C：

聚乳酸与聚苯乙烯熔融共混。即可以用高分子量聚苯乙烯（Piccolastic，E-125，Hercules），也可以用低分子量聚苯乙烯（Piccolastic，D-100）。还可以用通用聚苯乙烯（Huntsman 聚苯乙烯208），结晶聚苯乙烯。将它们以不同的比例与聚乳酸在Brabender机中325°F下混合。

所用聚苯乙烯/聚乳酸的比例为100/0（对照组），90/10和72/25（Huntsman 208，通用聚苯乙烯）。

实例6C-7C

使用两种类型的聚对苯二甲酸乙二醇酯（Goodyear 出产的"Clearstuff"和Eastman 出产的Kodapak TN-0148）。将它们在90℃下干燥过夜，与聚乳酸在Brabender机中525°F下熔融共混几分钟。聚乳酸的熔体粘度下降。

实例8C-16C：

将实例2C-7C的聚丙烯、通用聚苯乙烯和聚对苯二甲酸乙二醇酯（Eastman出产）的对照物和共混物用Abbey研磨机研磨，压塑成约5密耳厚的薄膜。在约400°F温度下模制聚丙烯-聚乳酸薄膜，在250-300°F温度下制备聚苯乙烯-聚乳酸薄膜，在约525°F温度下模制聚对苯二甲酸乙二醇酯-聚乳酸薄膜。在50%相对湿度和23℃温度条件

下放置24小时后，用Instron 测试。对照组也用相似的方法处理。将压塑薄膜的试样放在Atlas 老化试验机中来测定耐候性，试验机是 102分钟太阳光照射和18分钟雨水循环。这些实例的结果列于表1C。

实例17C-19C

用聚（D,L-乳酸）制备的100%聚乳酸按上述方法制成三个试样，不同的是薄膜厚度为 10-15密耳。试验按照下述实例20C-27C 的方法进行，不同的是第二个试样是在50% 相对湿度和72°F 温度下暴露82小时后进行试验。

实例20C-27C ：

将高密度聚乙烯(HDPE，0.960g/cc) 与聚乳酸在Brabender Plasticorder中 151℃温度下熔融共混10分钟。高密度聚乙烯/ 聚乳酸的共混比例为100/0 （对照组）、90/10 、80/20 和50/50 。每种共混物制备二个试样。该共混物用Abbey 研磨机研磨，并压塑成 10-15密耳薄膜。该薄膜用Atlas 老化试样机51分钟碳弧光照射和 9分钟水喷溅来进行试验。温度从室温至 140°F 。本试样的拉伸强度、断裂伸长率和拉伸断裂的类型均列在表2C中。

实例28C-33C ：

将低密度聚乙烯(LDPE，0.917g/cc) 与聚乳酸在Brabender Plasticorder中 151℃温度下熔融共混10分钟。低密度聚乙烯/ 聚乳酸的共混比例为100/0 （对照组）、90/10 和50/50 。每种共混物制备二个试样。该试样按照实例20C-27C 的方法处理和测定。结果列于表2C。

实例34C ：

在带有机械搅拌器和氮气出入口的 500毫升、三颈圆底烧瓶中放入 180.7克L-丙交酯和40.2克外消旋D,L-丙交酯(Boehringer 和 Ingelheim、S级) 。将烧瓶的内含物在氮气吹扫下加热至 110℃，使丙交酯熔融，加入20.1克聚苯乙烯(Amoco R3,熔融指数为3.5g/10min) 。

当搅拌过夜并提前加热至 185℃温度下，聚苯乙烯充分溶胀并部分溶解。将温度降至 141℃温度，加入 0.2毫升无水辛酸亚锡溶液(0.2毫升/毫升甲苯)。停止搅拌，让丙交酯在 141℃温度下聚合三天。当停止搅拌后，高溶胀的聚苯乙烯浮在顶部。冷却较低处的聚丙交酯相，用差示扫描量热法(DSC)测定。试样的Tg较低，大约35℃，另外它的表观温度转化较小。压塑薄膜是透明的，无色和非常柔韧。这种结果表明在这样的条件下，聚苯乙烯是完全不连续形成结晶的。

实例35C：

聚乳酸与结晶聚苯乙烯辊压共混。共混物显示出聚苯乙烯分散在聚乳酸中的优异相容性。在双辊研磨机中，170℃温度下5%(重量)聚苯乙烯分散在90/10 的L-/外消旋D,L-丙交酯共聚物中。材料变得浊雾，并用热分析得知具有非常大的结晶度。该实例说明，在这样的条件下，聚苯乙烯很容易在聚乳酸中产生结晶。该材料的热分析(参见图13)表明在加热和冷却后，该材料仍是结晶的。

实例34C 和35C 说明，聚乳酸与环境非降解塑料共混，根据混合或共混所用的方法可获得混合物的最终性能。

所有类型的Brabender 熔融共混物都具有10微米或更小的不均匀小颗粒。在模拟老化试验之前、之后测定拉伸强度。在Atlas 老化试验机进行1248小时(52天)试验之后，所有聚丙烯试样都变白、特别脆而不能进行试验。聚丙烯试样在较短时间间隔后再进行试验，结果列于表1C。在Atlas 老化试验机中，大约 300小时老化试验后，试样具有明显的环境降解。

聚苯乙烯与聚乳酸的共混物在 300小时模拟老化试验后，具有环境降解。聚对苯二甲酸乙二醇酯共混物在大约 300小时试验后也具有可见的环境降解。

表1C: 在加速老化试验之前和之后薄膜的拉伸强度[a]

共混比例和材料	拉伸强度[b] /%伸长率		
	之前	之后（ 小时）	
		310	340
100/0 PP/PLA[c]	1665/61	585/1.6	494/1.7
90/10, PP/PLA	1568/51	954/3.2	346/--
75/25, PP/PLA	1124/14	370/1.1	254/1.0
100/0 PP/PLA[d]	3200/2.0	1066/1.0	--
90/10, PS/PLA	2350/2.0	582/1.0	--
75/25, PS/PLA	1493/1.6	484/1.0	--
100/0 PET/PLA[e]	3036/--	3509/3.0	--
90/10, PET/PLA	2147/--	1378/3.0	--
75/25, PET/PLA	2743/--	2041/3.0	--

（a）老化试验机， 102分钟阳光照射和18分钟雨水循环。

（b）0.05in/min，用Instron 试验机。

（c）Hercules聚丙烯825。

（d）Huntsman 208。

（e）Tennessee Eastman，Kodapak TN 0148。

在进行模拟老化试验之前和之后，测定了聚乳酸、高密度聚乙烯、低密度聚乙烯和它们的共混物的物理强度，结果列于表2C。

表 2C：在老化试验机中暴露之前和之后，聚乙烯 (PE)、聚乳酸 (PLA) 和它们的共混物的物理性能

塑料(a)	材料中聚合物/PLA的共混比例	老化试验(c) 暴露时间 小时	拉伸强度 psi	(d) 断裂伸长率 %	拉伸破坏的类型
100% PLA(e)	0/100	0	6,030	2.2	脆性
100% PLA	0/100	0(f)	5,670	2.1	脆性
100% PLA	0/100	82	太脆不能试验	—	脆性
100% HDPE(g)	100/0	0	3,540	8	延性
100% HDPE	100/0	233	1,400	1	脆性
HDPE/PLA	90/10	0	3,480	3	延性
HDPE/PLA	90/10	233	1,720	1	脆性
HDPE/PLA	80/20	0	3,180	4	脆性
HDPE/PLA	80/20	125	2,150	2	脆性
HDPE/PLA	50/50	0	2,720	2	脆性
HDPE/PLA	50/50	233	太脆不能试验	—	脆性
100% LDPE(h)	100/0	0	1,320	80	延性
100% LDPE	100/0	125	1,250	67	延性
LDPE/PLA	90/10	0	1,190	31	延性
LDPE/PLA	90/10	125	855	14	延性
LDPE/PLA	50/50	0	1,160	4	延性
LDPE/PLA	50/50	125	太脆不能试验	—	脆性

(a) 压塑薄膜，10-15 密耳厚。

(b) 在Brabender Plasticorder中 151℃温度下熔融共混15分钟。

(c) 每小时中51分钟碳弧光照射和 9分钟水喷撒循环。温度为室温
    至 140°F。

(d) 在应变曲线中最大伸长率。

(e) 聚（D,L-乳酸）〔η〕为1.16dl/g，25℃下，THF 中。

(f) 在50% 相对湿度和72°F 下暴露82小时后。

(g) 高密度聚乙烯，密度为0.960g/cc，熔融指数为0.6g/10min。

(h) 低密度聚乙烯，密度为0.917g/cc，熔融指数为0.25g/10min。

聚乳酸及其共混物比起纯低密度聚乙烯或高密度聚乙烯极易环境降解。高密度聚乙烯试样降解基本上没有失重，而高密度聚乙烯-聚乳酸共混物有失重，特别是用显微镜观察到聚乳酸暴露在薄膜的表面。高密度聚乙烯在光化学光线下暴露而降解，可用显微镜观察到。

纵观所有试样，当聚乳酸的百分含量上升时，在模拟老化试验之前和之后，拉伸强度下降。加入聚乳酸使聚丙烯、聚苯乙烯、聚对苯二甲酸乙二醇酯以及高和低密度聚乙烯的共混物更快地降。据估计，光化光线以及聚酯的水解使聚合物降解。共混物的球状，微观不均匀的小区域一定是聚乳酸，它们基本上是浸入的。因而，聚乳酸的水解较慢。通过控制聚乳酸的分布来利用水解较快地降解。这又与熔融共混时共混物的流变学有关。分散的不均匀小区表明混合的聚合物具有较的相容性。

在模拟的废碴埋填时，光线被隔挡了，对照组和共混物都显示了极慢的降解速度。当在试验期间，共混物的质量没有变化，而仅仅是水解，可使聚乳酸试样变白。

相反，向聚乳酸中加入少量非降解热塑性塑料制成例如聚丙烯、聚苯乙烯、聚对苯二甲酸乙二醇酯以及高和低密度聚乙烯的相容共混物，可使聚乳酸的降解速度变慢。较好的组合物中，聚乳酸的含量为80-99%

（重量）。

一般讲，环境降解组合物包括聚乳酸（聚丙交酯）的机械混合物和聚合物的共混物，该聚合物选自对苯二甲酸—乙二醇的缩聚物，苯乙烯、乙烯、丙烯、氯乙烯、乙酸乙烯酯、甲基丙烯酸烷基酯、丙烯酸烷基酯及其机械混合物的聚合物或共聚物。其它可能的组合物共混物列于下面本发明实施方案的讨论中。

共混物较好的是式 I 的聚乳酸（n 为 75-10,000 的整数）的机械混合物和选自聚苯乙烯、聚乙烯、聚对苯二甲酸乙二醇酯和聚丙烯的聚合物的共混物，其它组合物将在下面讨论。较好的组合物是其中含有聚乳酸为 5-50%（重量）的组合物。更好的组合物是聚乳酸含量为 10-20%（重量）。

选自上述的聚合物，也可以认为是加入的聚合物，可以单独使用或合并使用。聚合物不受上述的限制，因为其它类型的聚合物也可与聚乳酸相容。这些聚合物包括乙烯、丙烯、苯乙烯、氯乙烯、乙酸乙烯酯、甲基丙烯酸烷基酯和丙烯酸烷基酯的聚合物和共聚物。应当认为，在此所用术语共聚物包括由上述单体的混合物制备的聚合物。另外，上述的聚合物和共聚物的机械混合物也可应用于本发明。

第三实施方案还提供了制备组合物的方法，该方法包括提供聚乳酸，由下列选择聚合物，对苯二甲酸—乙二醇的缩聚物，苯乙烯、乙烯、丙烯、氯乙烯、乙酸乙烯酯、甲基丙烯酸烷基酯、丙烯酸烷基酯及其机械混合物的聚合物和共聚物；将聚合物共混，共混可以在原纸辊上熔融共混，或者用挤出机化合，或用其它机械设备进行共混。较好的是得到具有通式（I）的聚乳酸。

在此还提供了另一种制备本发明组合物的方法，该方法包括提供一种丙交酯，它选自 D-丙交酯、L-丙交酯、内消旋 D,L-丙交酯、外消旋 D,L-丙交酯及其混合物；选择一种聚合物，它选自苯乙烯、乙烯、对苯二

70

甲酸一乙二醇、丙烯、氯乙烯、乙酸乙烯酯、甲基丙烯酸烷基酯、丙烯酸烷基酯及其机械混合物的聚合物或共聚物。选定的丙交酯和聚合物混合并加热至丙交酯熔融并至少部分溶解聚合物。丙交酯至少有部分聚合得到聚丙交酯的共混物，最后是没有聚合的丙交酯单体和选定的聚合物。聚合反应较好的控制是测定残留丙交酯的量，并在所需程度上停止聚合反应。如果需要，聚合反应可以进行完全。附加的丙交酯单体、乳酸、丙交酯低聚物、乳酸低聚物及其混合物可以制备柔韧物的量作为增塑剂加入，以获得在第一通用实施方案所述的所需特性。

根据聚乳酸和所加聚合物的互溶性，它们的比例可在很大的范围内变化，这对本技术领域人员是显而易见的。溶解度又随混合的充分程度和混合温度而变化。将聚乳酸和加入的聚合物放入互溶剂溶液中可以均匀相容的，这种溶剂在许多工业方法中不能使用。机械混合如用原纸辊或挤出机熔融共混是较易实施的，但必须要控制它成为均匀相容，也就是需用高剪切以获得所需的均匀相容。既使均匀混合的不同聚合物也是不相容的，也就是它们分成相当大的不均匀区域，例如10-100微米或更大。这样得到"干酪"状混合物或很差性能的共混物。令人惊奇的是，聚乳酸很容易与许多其它聚合物（包括极性和非极性聚合物）共混相容。

聚乳酸与其它聚合物的熔融共混温度可变化，以调节聚乳酸与一种或多种加入的聚合物的比例。较低温度不能得到适当的溶解度，温度太高又使混合物分解。一般温度范围为 100-220℃，较好的范围为130-180℃。等同的标志是不同聚合物组分的熔融粘度。随着分子量的增加，粘度迅速增加。通过控制聚乳酸和加入的一种或多种聚合物的比例、温度、混合方式和时间，以及分子量，可获得多种混合物。例如，聚乳酸可以分散在加入的一种或多种聚合物中，或反之，并且分散相的大小和结构可有较大的变化，可由分散的球状至不同直径或长度的丝。这使得它们在环境中物理性能和降解时间在很大范围变化。聚乳酸与选定聚合

物的重量百分比例为99：1-1：99。

在丙交酯单体用于溶解加入的聚合物，然后丙交酯聚合时，混合和聚合的温度必须要适于丙交酯的相互共溶性和反应性。较高温度一般制成较低分子量聚乳酸。本发明的另一实施方案是在某一温度下混合，而在另一温度下聚合，以获得如上述讨论的分散相结构的改善。

在此的组合物可由熔融制备方法制成具有自撑结构的有用制品如一次性使用容器、餐具、线盘、盘子、饮料杯、一次性托盘、注射器、医用盘、包装膜等等。该组合物是有用的，它们具有常用塑料的特性并且可以取代塑料，还可环境降解。本组合物特别适用于仅一次性使用或在处理前短时使用的制品。

第四通用实施方案：

本发明的第四实施方案包括弹性的和与聚乳酸共混相容的冲击改性物。共混相容是指所有聚合物可与聚乳酸紧密混合，正如第三通用方案所讨论的。该混合可得到基本上均匀的共混物。

在此公开的环境降解组合物至少是部分环境降解的。组合物的聚乳酸部分比起共混物的较稳定部分分解的相当快，并使得共混物的物理性能劣化。例如，当组合物是带有小区域的紧密和均匀共混物时，物理性能的劣化破坏了原制备产物。本组合物可提供环境适用的材料，因为它们的物理劣化和降解比常用非降解塑料快得多。另外，因为组合物的大部分是聚乳酸和/或乳酸制得的丙交酯或低聚物，只剩下小部分是较慢降解的弹性体残余物（如嵌段聚酯）。这种残余物具有较高表面积，并且比本体产物更快地分解。

下列实例说明了聚乳酸(PLA)与Hytrel™的共混，Hytrel™是一种嵌段聚酯，它是聚对苯二甲酸丁二醇酯的结晶硬链段和聚醚二醇的软长链段的嵌段共聚物。聚乳酸与弹性体是可熔融相容的，并影响它的物理性能。

D-丙交酯是D-乳酸的二丙交酯或环状二聚物。类似地，L-丙交酯是L-乳酸的环状二聚物。内消旋D,L-丙交酯是D-和L-乳酸的环状二聚物。外消旋D,L-丙交酯是D-和L-丙交酯的50/50混合物。当在此单独使用时，术语"D,L-丙交酯"是指包括内消旋D,L-丙交酯或外消旋D,L-丙交酯。聚乳酸可由上述的一种或多种丙交酯制备。

实例1D：

不含有Hytrel™嵌段聚酯的聚丙交酯共聚物是用流水号为229,939的第二种通用实施方案的实例1B的方法制备的，并测试它的缺口冲击强度。结果列于表1D。为了进一步比较，第二通用实施方案的表1B列出了L-丙交酯与D,L-丙交酯其它比例的缺口冲击强度。

实例2D：

向250毫升三颈圆底烧瓶中称量装入10.96克D,L-丙交酯、108.86克L-丙交酯和5.27克Hytrel™4056嵌段聚酯(DuPont 制造，热塑性弹性体)，Hytrel™4056嵌段聚酯是一种聚酯弹性体，它的硬度为肖氏D，低的弯曲模量，较高的熔融粘度，熔融指数为7，比重为1.17，熔点为334°F，维卡软化温度为234°F，挤出温度为340-400°F。该烧瓶装有机械搅拌器和氮气进出口。内含物用油浴加热。Hytrel™嵌段聚酯在170℃温度下溶解在熔融丙交酯中；催化剂溶液的制备是，将10毫升辛酸亚锡溶解在60毫升甲苯中，并蒸馏出10毫升甲苯。将100微升催化剂溶液注入到丙交酯和Hytrel™嵌段聚酯的溶液中。该混合物在155℃温度和氮气下搅拌约64小时。

粘度立即增大，混合物变得混浊。产物是韧的并不透明。在155℃温度下压塑成8-9密耳厚的薄膜，测定拉伸性能，如表1D所示。

压塑成1/8英寸厚的板，并用2磅的摆锤来测定它们的缺口冲击强度。结果记录在表1D。可将数据与不含Hytrel™嵌段聚酯的实例1D相似的聚丙交酯共聚物相比较，表1D还有所谓中等冲击聚苯乙烯（实例7D）

的数据。

实例3D：

将 800.0克L-丙交酯和 202.3克外消旋D,L-丙交酯用与实例2D相似的方法，应用 1.0毫升催化剂溶液共聚合，没有加Hytrel™嵌段共聚物。丙交酯共聚物是透明和无色的。在另一聚合反应中， 104.0克L-丙交酯用 100微升催化剂熔融聚合。聚合物(L-PLA) 是白色、结晶的，当遇冲击时很容易产生裂纹。

将电加热的两辊磨机加热至 375°F ，然后将 8.4克Hytrel™嵌段聚酯和19.2克L-PLA 绑扎在辊上。向此加入 172.4克丙交酯共聚物。该混合物很易共混并从辊上除去，压塑，并按照实例2D的方法测试。结果列于表1D。

实例4D：

将80克实例3D丙交酯共聚物、10克实例3D L-PLA和10克Hytrel™ 4056嵌段聚酯按前述实例3D的方法用两辊压磨机共混。共混物按前述方法测试，结果记录在表1D。

实例5D

100克实例3D的共混物与20克Hytrel™ 4056嵌段聚酯进一步共混。混合物在辊上很容易混合，并且外表是非常相容的。按前述方法测定物理性能并记录在表1D中。

实例6D和7D：

将常用结晶聚苯乙烯和中等冲击聚苯乙烯进行测试，用于比较的对照组。

上述结果清楚地表明，聚丙交酯可以冲击改性。共混物比起对照组的结晶聚苯乙烯具有明显高的缺口冲击强度，而相比于中等冲击的聚苯乙烯，它的冲击强度略低或相同。本领域的技术人员不难看出表1D中的冲击强度数据可通过优选冲击改性剂的用量和类型来进一步改善。

在前述第三通用实施方案所述，因为聚丙交酯是与许多其它化合物和热塑性塑料共混相容的，冲击改性的聚丙交酯是属于聚丙交酯和弹性体的共混相容混合物。本技术领域专业人员也可得知，表1D的数据改善是由于共混物是注射成型，与压塑成型相反，因为前者常使试样取向，然后冲击强度有较大改善。

表 1D: 冲击改性的聚丙交酯的物理性能比较

实例号	组合物%(重量)			拉伸强度 psi(b,c)	伸长率% percent	正切模量 psi	缺口冲击强度 ft-lb/in.(c)
	丙交酯共聚物	L-丙交酯均聚物	Hytrel™(a)				
1D	80(d)	20	0	7,667	3.4	322,679	0.3-0.4
2D	95.8(e)	0	4.2(f)	8,636	3.1	359,409	0.40
3D	86.2(g)	9.6	4.2(h)	7,823	3.1	346,502	0.51
4D	80.0(g)	10.0	10.0(h)	---	---	---	0.53
5D	71.2(g)	7.9	20.9(h)	---	---	---	0.61
6D(i)	0	0	0	6,118	3.2	267,245	0.18
7D(j)	0	0	0	6,090	4	---	0.7

(a) DoPont制造，Hytrel 4056，热塑性聚酯弹性体。

(b) ASTM D882，7-15 密耳厚薄膜。

(c) 压塑试样。

(d) 对照组，90/10 的L,D-/L- 丙交酯共聚物。

(e) 91/9的L-D/L-丙交酯共聚物。

(f) 在 170℃聚合之前，Hytrel溶解在丙交酯单体中。

(f) 80/20 的L-D/L-丙交酯共聚物。

(h) 两辊压磨机，在 185~190℃共混。

(i) 对照组，结晶聚苯乙烯，熔融指数为1.7。

(j) 对照组，中等冲击聚苯乙烯。

本组合物是有用的热塑性塑料，可用常用的方法如挤出法和模压法来熔融加工。

共混物较好的是用式 I 的聚乳酸(n为75-10,000 的整数)与包括嵌段聚酯的聚合物的机械混合物。有用的组合物是聚乳酸含量为50-99%（重量）的组合物。较好的组合物的聚乳酸含量为70-80%（重量）。

制备组合物的一般方法的两种实施方案包括(1)将PLA 与可改善耐冲击性如嵌段聚酯的共混相容聚合物熔融共混、(2)在如实例2D所述的PLA聚合过程中的溶液共混。在聚合中Hytrel™嵌段聚酯溶解在PLA 中。所用聚乳酸较好的是具有通式 I。如果需要，增塑剂以可产生揉曲性的量加入到共混物中，它选自丙交酯单体、乳酸低聚物、乳酸及其混合物。加入增塑剂可获得附加的独特物理性能。正如在上述第一、二和三通用实施方案中讨论的。

Hytrel™嵌段聚酯/ 聚乳酸的混合物的显微镜测定表明，分散的Hytrel™嵌段聚酯是以几微米或小的小球状区域存在的。这种区域的大小是由混合条件如混合的时间、速度和温度决定的。

例如：一种或多种加到聚乳酸中的聚合物一般是小的非均相的区域（小于10微米），并且是亚微观的或溶解在聚乳酸中。此外，这种冲击改性剂一定是弹性的。

还没有得到任何具体的理论，但是据信本发明提供了聚乳酸的连续基体，该聚乳酸含有作为裂纹滞止剂的Hytrel 嵌段聚酯的紧密混合显微区域，因为该聚酯是与聚乳酸相容的热塑性弹性体。

为此目的，冲击改性剂必须是弹性的，并与不连续非均相的聚乳酸紧密结合。加入的聚合物为冲击改性剂应是热塑性弹性体，或可交联橡胶，以获得弹性性能。这样的实例有天然橡胶和苯乙烯- 丁二烯共聚物。

将测试材料放在水中 5个月，该材料比起没有放在水中的材料脆。此外，水变成酸性的，表明聚乳酸断裂成乳酸。进一步说明了、仅仅

是聚乳酸的降解比起Hytrel™嵌段聚酯/聚乳酸混合物要快。因而，Hytrel™嵌段聚酯也可以用来减慢聚乳酸的降解速度。

加入可与上述讨论的其它组分相容的第三组分，以改善相容性。当聚乳酸和冲击改性剂的相容性较差时，可加入第三组分来改善相容性。当第三组分可与其它两组分分别相容，并且这两组分（聚乳酸和冲击改性剂）不能很好相容时，通常要加入第三组分。这样做可以提高聚乳酸和弹性的冲击改性剂间的相互结合。但是，出人意料的是聚乳酸与其它类型聚合物（包括极性和非极性）有较大范围的相容性。这可参阅第三通用实施方案。

在此的组合物可用熔融加工法制成有用的制品如容器、餐具、浅盘、盘子、饮料杯、一次性使用盘、注射器、医用盘等等。该组合物特别适用于一次性使用的制品，或在废弃前短时使用的制品。

本发明上述讨论了各种具体实例和实施方案，应该理解本发明不应受说明的实例和实施方案限制，并在下面的权利要求的范围内可有多种变化。

图 1

图 2

图 3

拉伸强度 psi（纵轴）
低聚物百分含量（横轴）

图 4

弹性模量 1000psi（纵轴）
低聚物百分含量（横轴）

图5：没有退火的90/10 L-/D,L-丙交酯共聚物的DSC

温度（℃）

热流量（毫瓦）

没有淬火

淬火

图6：在70℃下 100分钟后，图1 试样的DSC

没有淬火

淬火

温度（℃）

溶解度（IU）

图7．图1 的退火共聚物的DSC

185°F 烘箱中过夜

没有淬火

温度 (℃)

热流量 (毫W)
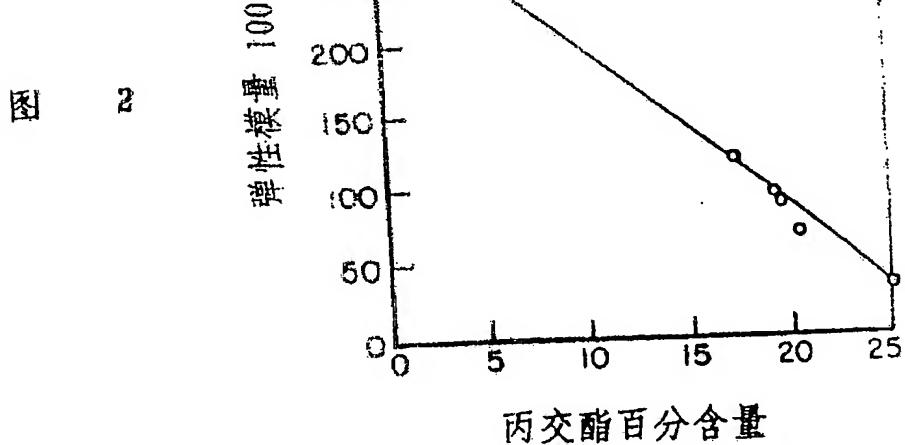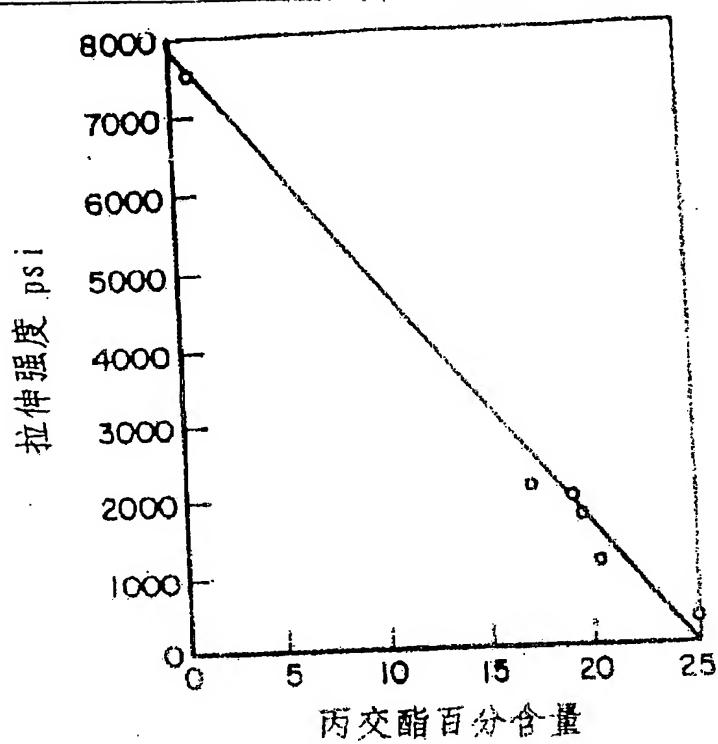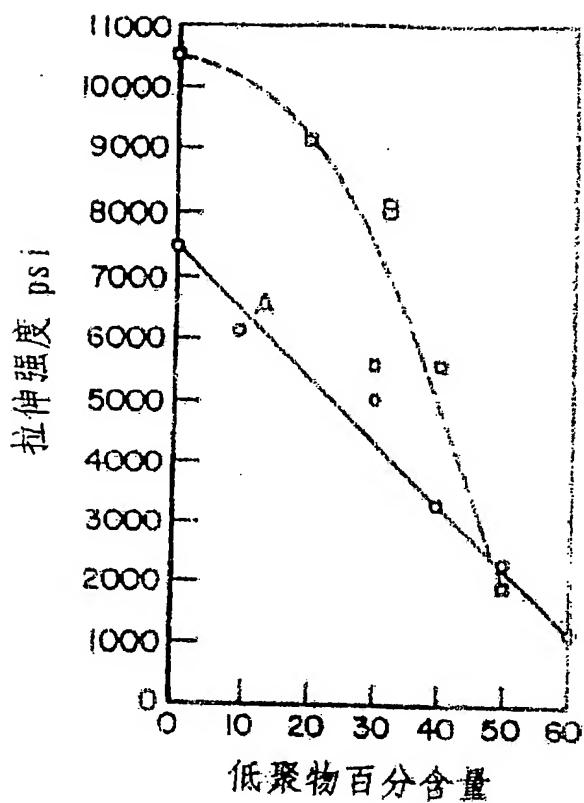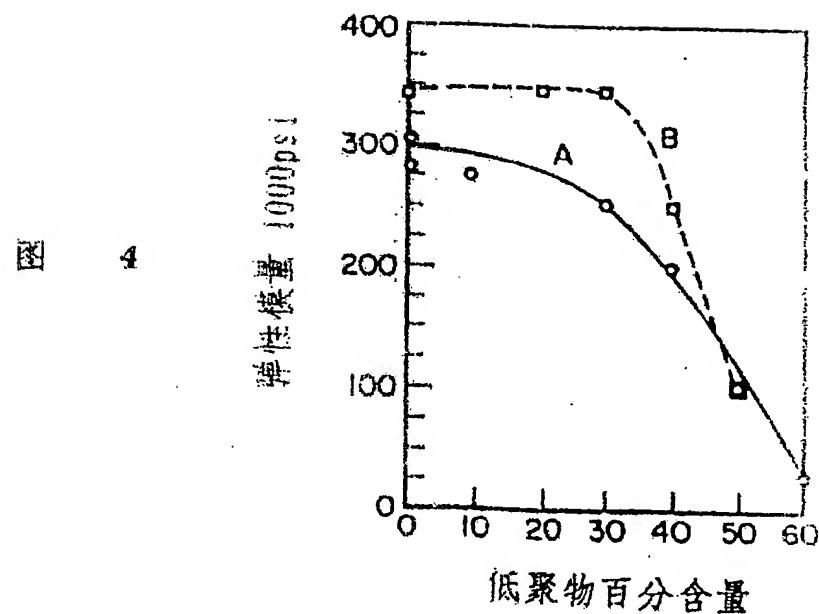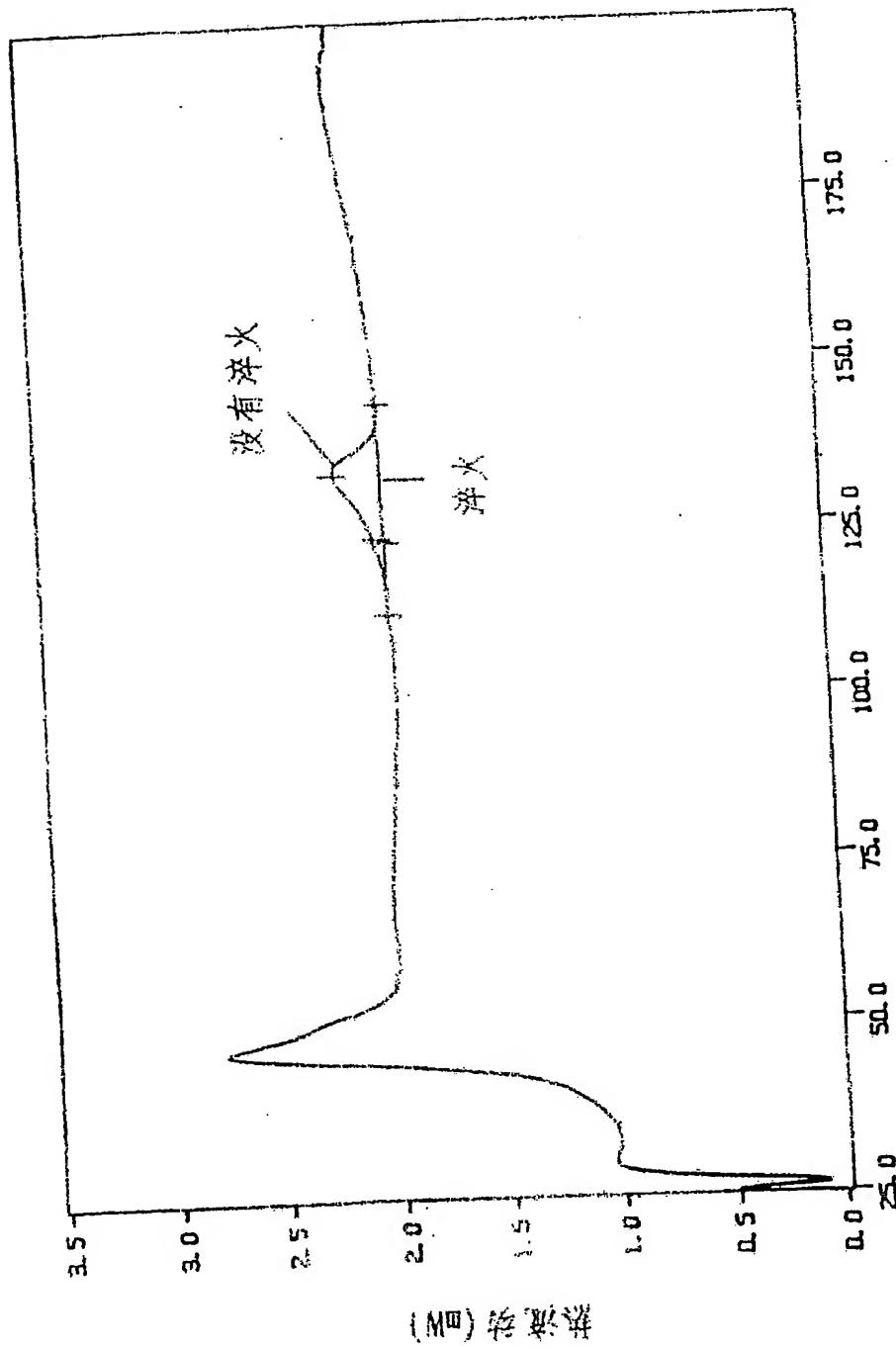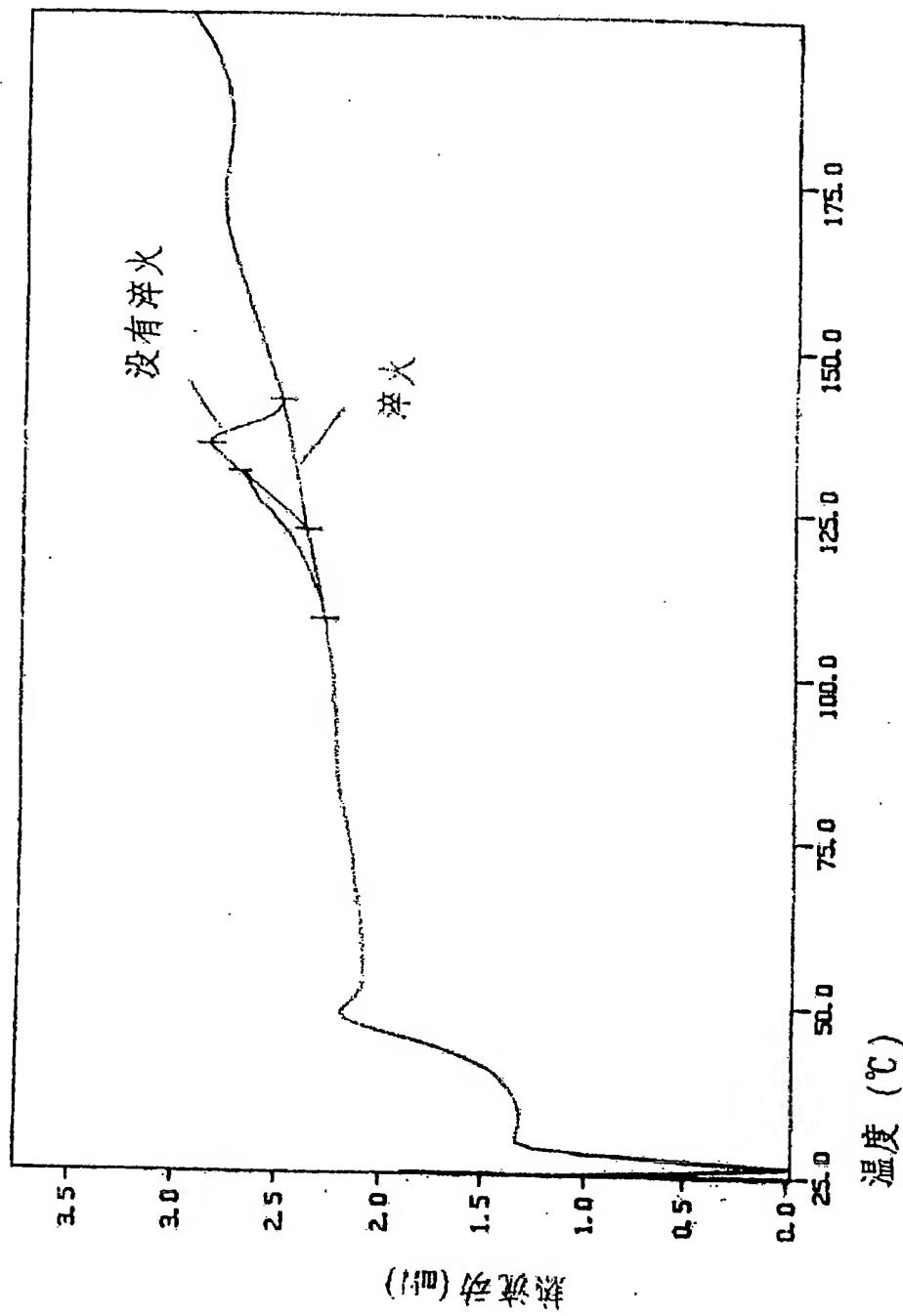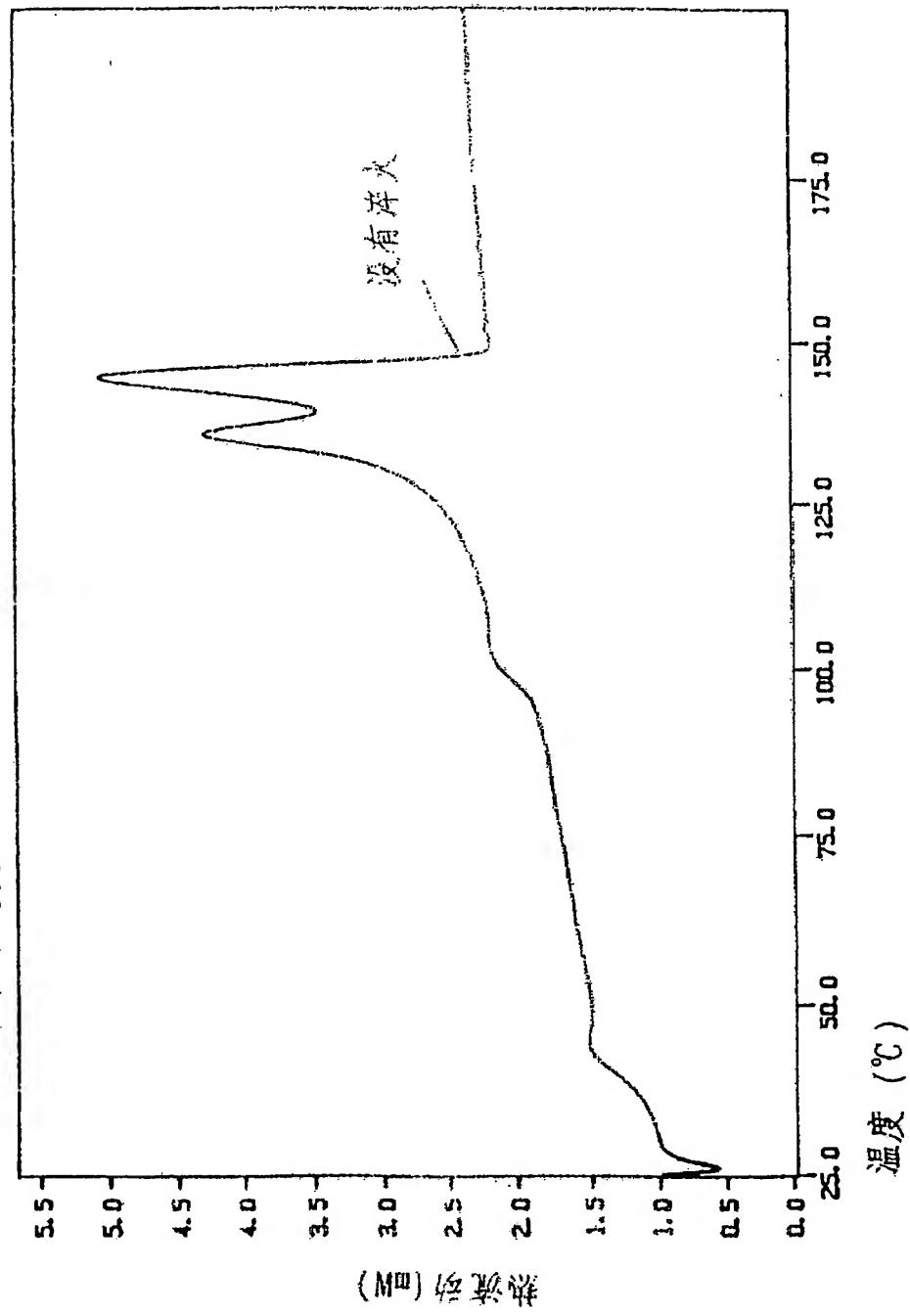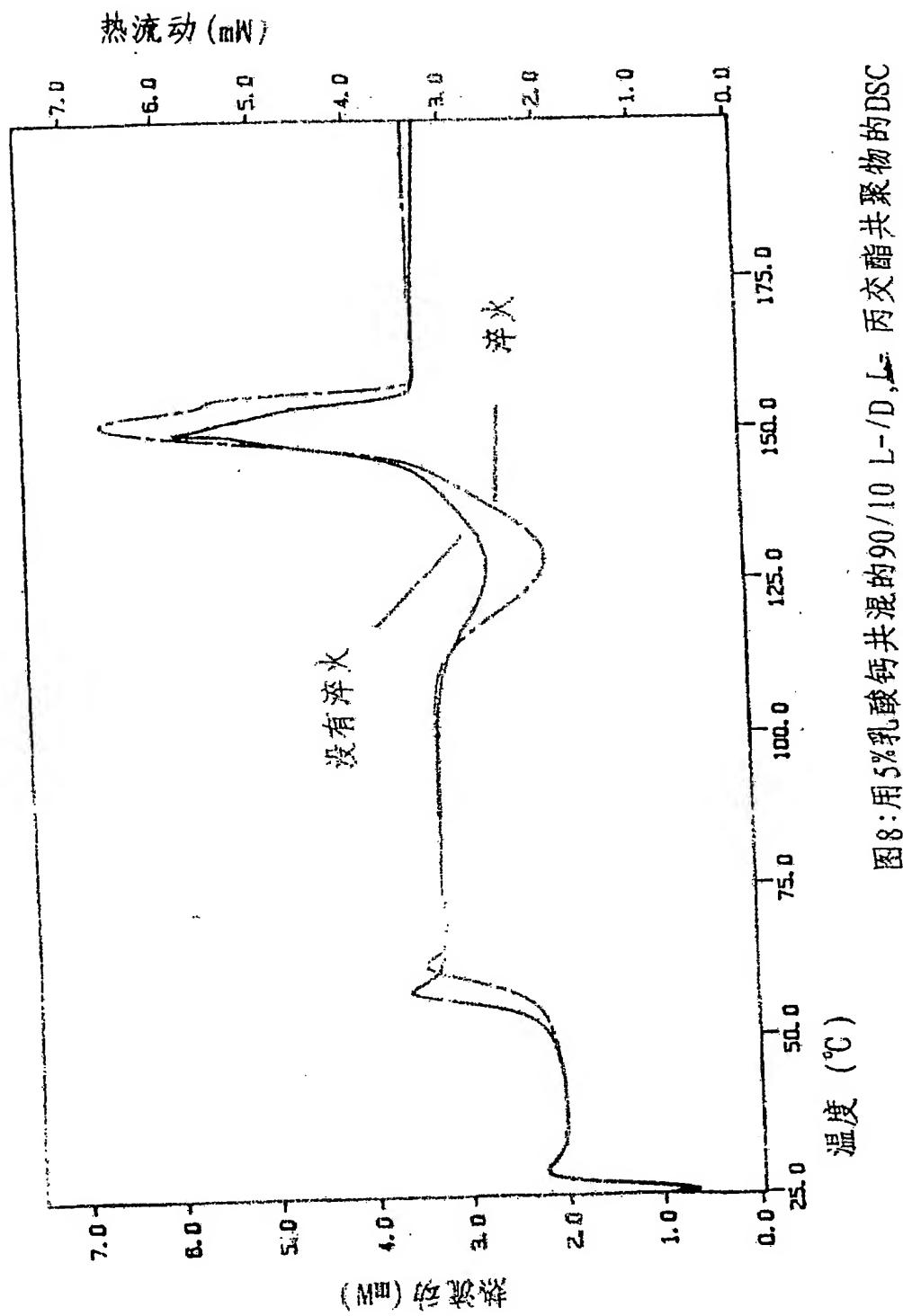
图8：用5%乳酸钙共混的90/10 L-/D,L- 丙交酯共聚物的DSC

粘度与剪切率

例 8 的丙交酯聚合物

剪切率（秒⁻¹） （X1000）

□ PS-200 C   + 例8-150 C
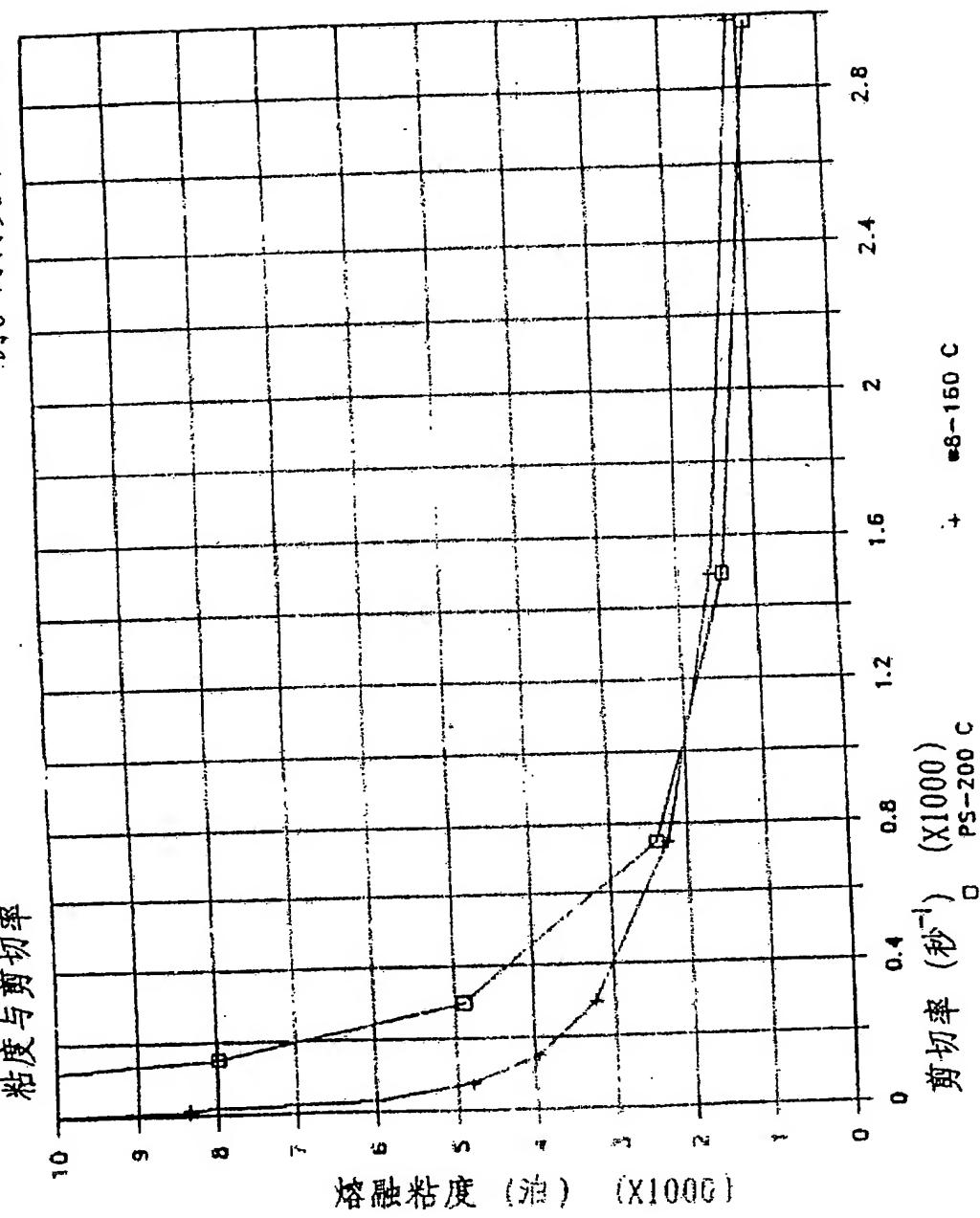
图9：聚苯乙烯与实例8 丙交酯聚合物的熔融粘度比较

热流动 (mW)

7.0　6.0　5.0　4.0　3.0　2.0　1.0　0.0

没有淬火

淬火

温度 (℃)

25.0　50.0　75.0　100.0　125.0　150.0　175.0

图10: 实例8 的材料

热流动 (mW)

7.0　6.0　5.0　4.0　3.0　2.0　1.0　0.0

热流动 (mW)

没有淬火

淬火

图11：100% L- 丙交酯的均聚物

温度（℃）

图12：共聚物和均聚物的共混物

热流动（mW）

温度（℃）

淬火

没有淬火

图13：用5%聚苯乙烯共混的90：10 L/D,L-丙交酯共聚物的DSC

热流动（mW）

温度（℃）

第一次加热

第二次加热

PCT

(51) International Patent Classification 4 : C08L 67/04, C08G 63/08	A1	(11) International Publication Number: **WO 90/01521** (43) International Publication Date: 22 February 1990 (22.02.90)

(21) International Application Number: PCT/US89/03380

(22) International Filing Date: 4 August 1989 (04.08.89)

(30) Priority data:

229,896	8 August 1988 (08.08.88)	US
229,939	8 August 1988 (08.08.88)	US
229,894	8 August 1988 (08.08.88)	US
317,391	1 March 1989 (01.03.89)	US
not furnished	2 August 1989 (02.08.89)	US
not furnished	2 August 1989 (02.08.89)	US
not furnished	2 August 1989 (02.08.89)	US
not furnished	2 August 1989 (02.08.89)	US

(71) Applicant: BATTELLE MEMORIAL INSTITUTE [US/US]; 505 King Avenue, Columbus, OH 43201-2693 (US).

(72) Inventors: SINCLAIR, Richard, G. ; 985 Kenway Court, Columbus, OH 43220 (US). PRESTON, Joseph, R. ; 4093 N. State Route 257, Radnor, OH 43066 (US).

(74) Agents: SHAWEKER, Kenneth, E. et al.; Battelle Memorial Institute, 505 King Avenue, Columbus, OH 43201-2693 (US).

(81) Designated States: AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CF (OAPI patent), CG (OAPI patent), CH (European patent), CM (OAPI patent), DE (European patent), DK, FI, FR (European patent), GA (OAPI patent), GB (European patent), HU, IT (European patent), JP, KP, KR, LK, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL (European patent), NO, RO, SD, SE, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent).

Published

With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: DEGRADABLE THERMOPLASTIC FROM LACTIDES
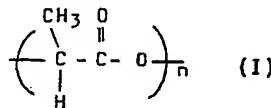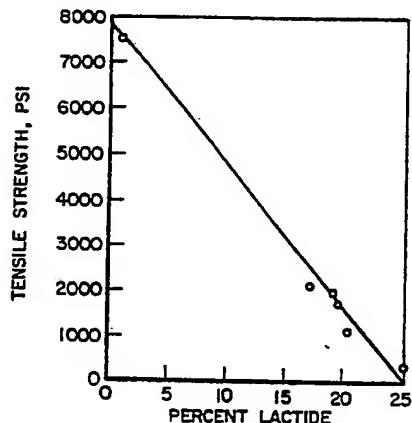
(57) Abstract

Biodegradable compositions of L-lactide, D-lactide, meso D,L-lactide, and racemic D,L-lactide which are suitable for pliable films and other packaging applications are prepared by polymerizing L-lactide, D-lactide, D,L-lactide or mixtures thereof using a catalyst at controlled conditions to allow the polymer in the composition to be plasticized by unreacted lactide monomer. Environmentally biodegradable polymer, composition and process for a polymer and a composition. The biodegradable polymer comprises polymerized lactic acid units of structure (I), where n is an integer between 75 and 10,000 and the alpha carbon is a mixture of L- and D-configurations where the unoriented polymer has a tensile strength of at least 5,000 psi and tangent modulus of at least 200,000 psi. Another embodiment provides for an environmentally degradable composition comprising blends of a physical mixture of polylactic acid, and a polymer selected from the group consisting of the polymers of ethylene terephthalate, a polymer or copolymer of styrene, ethylene, propylene, vinyl chloride, vinyl acetate, alkyl methacrylate, alkyl acrylate, and physical mixtures thereof.

DEGRADABLE THERMOPLASTIC FROM LACTIDES

The present application is derived from and claims priority of the following eight U.S. applications: The application entitled PLIABLE BIODEGRADABLE PACKAGING THERMOPLASTICS FROM LACTIDES having Serial No.
5 07/229,896, filed August 8, 1988; and the application entitled BIODEGRADABLE REPLACEMENT OF CRYSTAL POLYSTYRENE having Serial No. 07/229,939, filed August 8, 1988; and the application entitled BLENDS OF POLYLACTIC ACID having Serial No. 07/229,894, filed August 8, 1988; and the application entitled DEGRADABLE IMPACT MODIFIED POLYLACTIDES
10 having Serial No. 07/317,391, filed March 1, 1989; and the application PLIABLE BIODEGRADABLE PACKAGING THERMOPLASTICS FROM LACTIDES having attorney docket number PF 2767-1, filed July 31, 1989; and the application entitled BIODEGRADABLE REPLACEMENT OF CRYSTAL POLYSTYRENE having attorney docket number PF 2771-1, filed July 31, 1989; and the
15 application entitled BLENDS OF POLYLACTIC ACID having attorney docket number PF 2772-1, filed July 31, 1989; and the application entitled DEGRADABLE IMPACT MODIFIED POLYLACTIDES having attorney docket number PF 2781-1, filed on July 31, 1989. All of the above applications having Battelle Memorial Institute as assignee.

20 FIELD OF THE INVENTION

In a first embodiment, the present invention relates to plasticized polymers of L-lactide, D-lactide, D,L-lactide and mixtures thereof suitable for packaging applications conventionally served by nondegradable plastics (e.g. polyethylene). The first embodiment
25 further relates to a method for producing pliable films and other packaging items and to the unique product thereof. The invention has utility in producing a product that has the characteristics of the usual plastics yet is biodegradable.

In a second embodiment, the invention discloses a material and
30 process of preparing it which is an offset, that is a replacement for crystal polystyrene, sometimes known as orientable polystyrene or OPS. The material is an offset for the OPS but is composed of a polyester

- 2 -

capable of biodegrading in the environment over approximately 1 years
time. The material is a polyester, comprised of polymerized lactic
acid, prepared from either D-lactic acid or L-lactic acid, and D,L-
lactic acid. The ratio of the two polymerized monomer units, the
5 process treatment and in some cases certain adjuvants, determine the
precise physical properties required for the exacting requirements of
an OPS offset. Thus, at approximately a ratio of 90/10, L-lactic/D,L-
lactic acid, the polymerized lactic acid (PLA) is a well behaved
thermoplastic that is clear, colorless, and very stiff. As such it is
10 very suitable for preparing films, foams, and other thermoformed items
of disposable or one-way plastic. Having served its purpose as a
packaging plastic, the PLA slowly environmentally biodegrades to
innocuous products when left on or in the environment. This harmless
disappearance can help alleviate the mounting problems of plastic
15 pollution in the environment.

In a third embodiment, the invention relates to the blending of
conventional thermoplastics with polylactic acid. This provides novel,
environmentally degradable thermoplastics. The environmentally
degradable thermoplastics are useful in a wide variety of applications.
20 The third embodiment further relates to a method for producing
pliable films and other packaging items and to the unique product
thereof. The invention has utility in producing a product that has the
characteristics of the usual plastics yet is environmentally
degradable.

25 A fourth embodiment of the invention relates to the blending of
compatible elastomers with polylactides. This provides impact-
resistant modified polylactides that are useful in a wide variety of
applications including those where impact-modified polystyrene would be
used.

30 The fourth embodiment further relates to a method for producing
packaging items and to the unique product thereof. The invention has
utility in making a product that has the characteristics of the usual
impact-resistant plastics yet is environmentally degradable.

BACKGROUND OF THE INVENTION

There is a need for an environmentally biodegradable packaging thermoplastic as an answer to the tremendous amounts of discarded plastic packaging materials. U.S. plastic sales in 1987 were 53.7
5   billion pounds of which 12.7 billion pounds were listed as plastics in packaging. A significant amount of this plastic is discarded and becomes a plastic pollution that is a blot on the landscape and a threat to marine life. Mortality estimates range as high as 1-2 million seabirds and 100,000 marine mammals per year.

10   A further problem with the disposal of plastic packaging is the concern for dwindling landfill space. It has been estimated that most major cities will have used up available landfills for solid waste disposal by the early 1990's. Plastics comprise approximately 3 percent by weight and 6 percent of the volume of solid waste.

15   One other disadvantage of conventional plastics is that they are ultimately derived from petroleum, which leaves plastics dependent on the uncertainties of foreign crude oil imports. A better feedstock would be one that derives from renewable, domestic resources.

However, there are good reasons for the use of packaging plastics.
20   They provide appealing aesthetic qualities in the form of attractive packages which can be quickly fabricated and filled with specified units of products. The packages maintain cleanliness, storage stability, and desirable qualities such as transparency for inspection of contents. These packages are known for their low cost of production
25   and chemical stability. This stability, however leads to very long life of plastic, so that when its one time use is completed, discarded packages remain on, and in, the environment for incalculably long times.

The polymers and copolymers of lactic acid have been known for
30   some time as unique materials since they are biodegradable, biocompatible and thermoplastic. These polymers are well behaved thermoplastics, 100 percent, truly biodegradable in an animal body via hydrolysis over a time period of several months to a year. In a wet environment they begin to show degradation after several weeks and disappear in
35   about a year's time when left on or in the soil or seawater. The

- 4 -

degradation products are lactic acid, carbon dioxide and water, all of which are harmless.

In practice, lactic acid is converted to its cyclic dimer, lactide, which becomes the monomer for polymerization. Lactic acid is
5   potentially available from inexpensive feedstocks such as cornstarch or corn syrup, by fermentation, or from petrochemical feedstocks such as ethylene. Lactide monomer is conveniently converted to resin by a catalyzed, melt polymerization, a general process well-known to plastics producers. By performing the polymerization from an inter-
10 mediate monomer, versatility in the resin composition is permitted. Molecular weight can be easily controlled. Compositions can be varied to introduce specific properties.

Homopolymers and copolymers of various cyclic esters such as glycolide, lactide, and the lactones have been disclosed in numerous
15 patents and scientific publications. Early patents disclosed processes for polymerizing lactic acid, lactide, or both, and did not achieve high molecular weight polymers with good physical properties, and the polymer products were frequently tacky, sticky materials, without good physical properties. See, for example, U.S. Patents 1,995,970;
20 2,362,511; and 2,683,136. The Lowe patent, U.S. Patent 2,668,162 first teaches the use of pure glycolide and lactide to achieve high molecular weight polymers and copolymers of lactide. Lactide is the dilactone of lactic acid and is an internal ester of lactic acid. When lactide is formed, byproduct water is eliminated, permitting the lactide
25 subsequently to be ring-opened polymerized to linear polyester of high molecular weight without tedious condensation methods. Copolymerization of lactide and glycolide imparted toughness and improved thermoplastic processability as compared to the homopolymers. Polymers and copolymers of excellent physical properties were obtained
30 by using the intermediate, lactide, to form PLA. Copolymers of lactide and glycolide are disclosed by the Lowe patent which are tough, clear, cold-drawable, stretchable, and capable of forming at 210 C into self-supporting films.

Similar disclosures in the patent and other literature developed
35 the processes of polymerization and copolymerization of lactide to

- 5 -

produce very strong, crystalline, orientable, stiff polymers which were
fabricated into fibers and prosthetic devices that were biodegradable
and biocompatible, sometimes called absorbable. The polymers slowly
disappeared by hydrolysis. See, for example, U.S. Patents 2,703,316;
5   2,758,987; 3,297,033; 3,463,158; 3,531,561; 3,620,218; 3,636,956;
3,736,646; 3,797,499; 3,839,297; 3,982,543; 4,243,775; 4,438,253;
4,496,446; European Patent Application 0146398, International Applica-
tion WO 86/00533, and Offenlegundsschrift 2,118,127.

Other patents teach the use of these polymers as stiff surgical
10 elements for biomedical fasteners, screws, nails, pins, and bone
plates. See, for example, U.S. Patents 3,739,773; 4,060,089; and
4,279,249.

Controlled release devices, using mixtures of bioactive substances
with the polymers and copolymers of lactide and/or glycolide, have been
15 disclosed. See, for example, U.S. Patents 3,773,919; 3,887,699;
4,273,920; 4,419,340; 4,471,077; 4,578,384; 4,728,721; R.G. Sinclair,
Environmental Science & Technology, 7 (10), 955 (1973). R.G. Sinclair,
Proceedings, 5th International Symposium on Controlled Release of
Bioactive Materials, 5.12 and 8.2, University of Akron Press, 1978.
20 These applications of lactide polymers and copolymers required tough,
or glassy materials, that were grindable and did not disclose physical
properties for obvious use in thermoplastic packaging materials.

Some mention has been disclosed in the prior art for use of
lactide copolymers for obvious packaging applications. Thus, in the
25 aforementioned patent to Lowe, clear, self-supporting films are noted
of a copolymer of lactide and glycolide. In U.S. Patent 2,703,316
lactide polymers are described as film formers, which are tough and
orientable. "Wrapping tissue" was disclosed that was tough, flexible,
and strong, brittle, or pliable. However, to obtain pliability the
30 polylactide must be wet with volatile solvent, otherwise, stiff and
brittle polymers were obtained. The lactide monomer is specified as
having a melting point greater than 120 C. L-lactide monomer melts at
95 C and D,L-lactide melts at 128 C. This is an example of the prior
art which teaches special modifications of lactide polymers to obtain
35 pliability. Thus, in U.S. Patent 3,021,309, lactides are copolymerized

- 6 -

with delta valerolactone and caprolactone to modify lactide polymers
and obtain tough, white, crystalline solids. Soft, solid copolymer
compositions are mentioned only with the copolymer of caprolactone and
2,4-dimethyl-4-methoxymethyl-5-hydroxypentanoic acid lactone, not with
5 lactide compositions. U.S. Patent 3,284,417 relates to the production
of polyesters which are useful as plasticizers and intermediates for
the preparation of elastomers and foams. This patent excludes lactides
and uses compositions based on 7 to 9 membered ring lactones, such as
epsilon caprolactone, to obtain the desired intermediates. No tensile
10 strength, modulus, or percent elongation data are given. U.S. Patent
3,297,033 teaches the use of glycolide and glycolide-lactide copolymers
to prepare opaque materials, orientable into fibers suitable for
sutures. It is stated that "plasticizers interfere with crystallinity,
but are useful for sponge and films". Obvious in these disclosures is
15 that the lactide polymers and copolymers are stiff unless plasticized.
This is true also of U.S. Patent 3,736,646, where lactide-glycolide
copolymers are softened by the use of solvents such as methylene-
chloride, xylene, or toluene. In U.S. Patent 3,797,499 copolymers of
L-lactide and D,L-lactide are cited as possessing greater flexibility
20 in drawn fibers for absorbable sutures. These fibers have strengths
greater than 50,000 psi with elongation percentages of approximately 20
percent. Moduli are about one million psi. These are still quite
stiff compositions compared to most flexible packaging compositions,
reflecting their use for sutures. U.S. Patent 3,844,987 discloses the
25 use of graft and blends of biodegradable polymers with naturally
occurring biodegradable products, such as cellulosic materials, soya
bean powder, rice hulls, and brewer's yeast, for articles of manufac-
ture such as a container to hold a medium to germinate and grow seeds
or seedlings. These articles of manufacture are not suitable for
30 packaging applications.
      U.S. Patent 4,620,999 discloses a biodegradable, disposable bag
composition comprised of polymers of 3-hydroxybutyrate and 3-hydroxy-
butyrate/3-hydroxyvalerate copolymer. Lactic acid, by comparison, is
2-hydroxy propionic acid. U.S. Patent 3,982,543 teaches the use of
35 volatile solvents as plasticizers with lactide copolymers to obtain

pliability. U.S. Patents 4,045,418 and 4,057,537 rely on copolymeriza-
tion of caprolactone with lactides, either L-lactide, or D,L-lactide,
to obtain pliability. U.S. Patent 4,052,988 teaches the use of poly
(p-dioxanone) to obtain improved knot tying and knot security for
5   absorbable sutures. U.S. Patents 4,387,769 and 4,526,695 disclose the
use of lactide and glycolide polymers and copolymers that are deform-
able, but only at elevated temperatures. European Patent Application
0108933 using a modification of glycolide copolymers with polyethylene
glycol to obtain triblock copolymers which are taught as suture
10   materials. As mentioned previously, there is a strong consensus that
pliability is obtained in lactide polymers only by plasticizers which
are fugitive, volatile solvents, or other comonomer materials.
        Copolymers of L-lactide and D,L-lactide are known from the prior
art, but citations note that pliability is not an intrinsic physical
15   property. U.S. Patent 2,758,987 discloses homopolymers of either L- or
D,L-lactide which are described as melt-pressable into clear, strong,
orientable films. The properties of the poly-L-lactide are given as:
tensile strength, 29,000 psi; percent elongation, 23 percent, tensile
modulus 710,000 psi. The poly-D,L-lactide properties were: 26,000 psi
20   tensile strength; 48 percent elongation; and a tensile modulus of
260,000 psi. Copolymers of L- and D,L-lactide, that is copolymers of
L- and D,L-lactic acid, are disclosed only for a 50/50 by weight
mixture. Only tack point properties are given (Example 3). It was
claimed that one antipodal (optically active, e.g., L-lactide) monomer
25   species is preferred for the development of high strength. The
homopolymers of L-lactide and D,L-lactide, as well as the 75/25, 50/50,
and 25/75, weight ratio, of L-/D,L-lactide copolymers are exampled in
U.S. Patent 2,951,828 that discloses the bead polymerization of alpha-
hydroxy-carboxylic acids. The copolymers have softening points of 110-
30   135 C. No other physical property data are given relating to stiffness
and flexibility except for physical properties relating to bead size
and softening points in the 110 - 135 C range. The 95/5, 92.5/7.5,
90/10, and 85/15, weight ratio, of L-lactide/D,L-lactide copolymers are
cited in U.S. Patents 3,636,956 and 3,797,499. They are evaluated as
35   filaments from drawn fibers and have tensile strengths in excess of

50,000 psi, moduli of about one million, and percent elongations of
approximately 20 percent. Plasticizers, the same as in U.S. Patent
3,636,956, above, were used to impart pliability. A snow-white,
obviously crystalline polymer, is cited in Offenlegundsschrift

5   2,118,127 for a 90/10, L-lactide/D,L-lactide copolymer. No physical
properties were given for this copolymer. The patent teaches the use
of surgical elements.

U.S. Patents 3,297,033; 3,463,158; 3,531,561; 3,636,956;
3,736,646; 3,739,773; and 3,797,499 all disclose lactide polymers and

10   copolymers that are strong crystalline, orientable polymers suitable
for fibers and suture materials. These disclosures teach the use of
highly-crystalline materials, which are oriented by drawing and
annealing to obtain tensile strengths and moduli, typically, greater
than 50,000 psi and 1,000,000 psi, respectively. Although formability

15   is mentioned into a variety of shaped articles, physical properties of
unoriented extrudates and moldings are not mentioned. For example,
U.S. Patent 3,636,956 teaches the preparation of a 90/10 weight ratio
of L-lactide/D,L-lactide and drawn, oriented fibers are cited.
However, it is preferred in this disclosure to use pure L-lactide

20   monomer for greater crystallinity and drawn fiber strength.

U.S. Patent 3,797,499 teaches the copolymerization of 95/5 weight
ratio, of L-lactide/D,L-lactide (Example V); however, the material is
formed into filaments. In column 5, line 1 Schneider teaches against
enhanced properties in the range provided in the present invention.

25   Plasticizers such as glyceryl triacetate, ethyl benzoate and diethyl
phthalate are used.

U.S. Patents 3,736,646; 3,773,919; 3,887,699; 4,273,920;
4,471,077; and 4,578,384 teach the use of lactide polymers and
copolymers as sustained-drug release matrices that are biodegradable

30   and biocompatible. Again, physical properties of the polymers from
ordinary thermoforming methods such as film extrusion or molding are
not mentioned.

Of particular interest, U.S. patent 4,719,246 teaches the blending
of homopolymers of L-lactide, D-lactide, polymers or mixtures thereof;

35   and copolymers of L-lactide or D-lactide with at least one nonlactide

- 9 -

comonomer.   The blending is intended to produce compositions having interacting segments of poly(L-lactide) and poly(D-lactide).

Canadian Patent 808,731 cites the copolymers of L- and D,L-lactide where a divalent metal of Group II is part of the structure.   The

5   90/10, L-/D,L-lactide copolymer (Example 2) and the L-lactide homopolymer were described as "suitable for films and fibers".   The 90/10 copolymer is described as a snow-white copolymer and the homopolymer of L-lactide can be molded to transparent films.   (The more crystalline polymer should be the opaque, or snow-white material, which is the

10 homopolymer.)   The patent discloses "the fact that the novel polylactides of the present invention contain the metallic component of the catalyst in the form of a lactate is believed to be of significance".   Furthermore, "the polylactides find utility in the manufacture of films and fibers which are prepared by conventional thermoplastic resin manu-

15 facturing methods".   No physical property data are given on the strength and flexibility of the films.

Canadian Patent 863,673 discloses compositions of L-lactide and D,L-lactide copolymers in the ratios of 97/3, 95/5, 92.5/7.5, 90/10, and 85/15 ratios of L-/D,L-lactide, respectively.   These were all

20 characterized as drawn filaments for surgical applications.   Tensile strength, approximately 100,000 psi, was high, elongation was approximately 20 percent and plasticizers were mentioned to achieve pliability.   D,L-lactide compositions of less than 15 weight percent are claimed.

25   Canadian Patent 923,245 discloses the copolymers of L- and D,L-lactide (Example 15).   The 90/10 copolymer is described as a snow white polylactide.   The polylactides prepared by the methods of the patent are stated to have utility in the manufacture of films or fibers prepared by conventional thermoplastic resin fabricating methods.

30   U.S. Patent 4,719,246 teaches the use of simple blending of poly L-and poly (D-lactide), referred to as poly (S-lactide) and poly (R-lactide), polymers of mixtures thereof; and copolymers of L-lactide or D-lactide with at least one nonlactide comonomer.   The examples are all physical mixtures.   The special properties of the "interlocking" stem

35 from racemic compound formation (cf. "Stereochemistry of Carbon

- 10 -

Compounds", E. L. Eliel, McGraw-Hill, 1962, p. 45). Racemic compounds
consist of interlocked enantiomers, that is, the D and L forms (or R
and S) are bonded to each other by polar forces. This can cause a
lowering, or raising, of the crystalline melting points, depending on
5   whether the D to D (or L to L) forces are less, or greater, than the D
to L forces. Required of polymer racemic compounds to enhance the
effect (and stated in U.S. Patent 4,719,246, Column 4, line 48) are
homopolymers, or long chain lengths, of both D and L. The great
symmetry or regularity of these structures permit them to fit together,
10 or interlock, by very regular polar forces, either because they are the
same, or mirror images. This leads to considerable crystallinity. The
art of racemic compounds has a long history that goes back to classical
chemistry.

U.S. patent 4,661,530, discloses the mixtures of a poly (L-lactic
15 acid) and/or poly (D,L-lactic acid) and segmented polyester urethanes
or polyether urethanes. Biodegradable materials are formed that are
useful in synthetic replacements of biological tissues and organs in
reconstructive surgery.

Nowhere in the prior art is it disclosed that lactide polymers,
20 are capable of pliable, highly-extensible compositions by the use of
lactide monomers, lactic acid, or oligomers of lactic acid or lactide
as the plasticizer. None of the prior compositions are suitable for
well-defined packaging needs of the thermoplastic polymers' industry.

It will be appreciated by those skilled in the art that duplicat-
25 ing the properties of one thermoplastic with another is not predict-
able. Thus, with crystal polystyrene, or OPS, there are exacting
requirements for satisfactory performance of the polystyrene, which has
been developed over many years to meet manufacturing and end-use
specifications of OPS grades.

30 BRIEF DESCRIPTION OF THE INVENTION

The general teaching of the invention, and first embodiment, is
that homopolymers of L-lactide, D-lactide, and D,L-lactide and
copolymers of mixtures thereof that have been plasticized with lactide
monomer(s), lactic acid or oligomers of lactide or of lactic acid have

utility as well behaved thermoplastics which can mimic properties of
the usual environmentally nondegradable plastics, (e.g., the properties
of polyethylene and the like). This composition has the formula:

$$\left(-\underset{\alpha}{\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}} - \overset{\overset{\displaystyle O}{\|}}{C} - O-\right)_n \qquad I$$
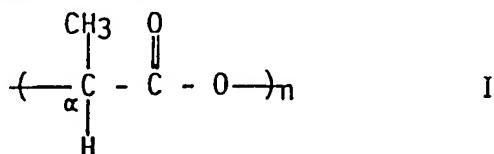
and is intimately plasticized with a plasticizer selected from the
group consisting of lactide, lactic acid, oligomers of lactic acid, and
mixtures thereof. The oligomers of lactic acid further are preferably
represented by the formula II, where m is an integer: $2 \leq m < 75$.
However, m is preferably $2 \leq m \leq 10$. The plasticizer preferably
comprises from 2 to 60 weight percent of the polymer. The polymers may
be derived from monomers of lactide selected from the group consisting
of L-lactide, D-lactide, meso D,L-lactide and mixtures thereof.
Preferably n is $150 \leq n \leq 20,000$.

$$\left(-\underset{\alpha}{\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}} - \overset{\overset{\displaystyle O}{\|}}{C} - O-\right)_m \qquad II$$
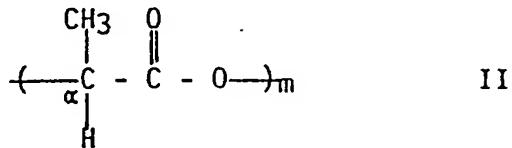
Lactide monomer can be present in an amount of from 5 to 40
weight percent of the polymer while lactide oligomer or lactic acid and
its oligomers may be present in an amount of from 2 to 60 weight
percent. This composition allows many of the desirable characteristics
of polyethylene such as pliability, transparency, and toughness.

Further provided is a process for producing the biodegradable
composition. The process includes the steps of mixing, heating, and
melting one or more lactide monomers and catalyst; polymerizing the
monomers of the solution to form a polymer at a temperature
sufficiently low to allow the polymerization reaction to be stopped
prior to complete polymerization; monitoring the level of monomer; and
stopping the reaction prior to complete polymerization at an amount of
monomer determined by the monitoring; so that unreacted monomer is
trapped in association with the polymer.

Further provided is a process for producing a plasticized polymer
of polylactic acid that comprises mixing, heating, and melting one or

- 12 -

more lactide monomers and a catalyst; polymerizing the monomers of the solution to form a polymer without stopping the reaction; and incorporating plasticizer into the polymer whereby the plasticizer is selected from the group consisting of D-lactide, L-lactide, meso D,L-
5   lactide, lactic acid, oligomers of lactic acid, and mixtures thereof.

A second embodiment of the invention includes a process for producing an environmentally biodegradable composition and an environmentally biodegradable composition useful as a replacement for polystyrene comprising polylactic acid units of the formula I where n
10   is an integer between 75 and 10,000 and the alpha carbon is a mixture of L- and D-configurations with a preponderance of either D- or L-units, wherein the polymer is prepared from L-lactide or D-lactide, at 85 to 95 parts by weight, and D,L-lactide at 15 to 5 parts by weight, where the unoriented polymer has a tensile strength of at least 5000
15   psi and tangent modulus of at least 200,000 psi and dispersed plasticizer of 0.1 - 5 weight percent.

A third embodiment of the invention teaches the process for producing an environmentally degradable composition and an environmentally degradable composition comprising blends of a physical
20   mixture of polylactic acid; and one or more polymers selected from the group consisting of a polymer of ethylene terephthalate, a polymer or copolymer of styrene, ethylene, propylene, vinyl chloride, vinyl acetate, alkyl methacrylate, alkyl acrylate, and physical mixtures thereof.

25   A fourth embodiment teaches the process for producing an environmentally degradable composition and an environmentally degradable composition is disclosed comprising blends of a physical mixture of polylactic acid and blend-compatible elastomers that provide improved impact resistance to the blended composition. Such an
30   elastomer may be, for example, a Hytrel™, a segmented polyester which is a block copolymer of hard crystalline segments of polybutylene terephthalate and soft long chain segments of polyether glycol. One example is known by the trade name as Hytrel™ 4056 (DuPont) segmented polyester.

- 13 -

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a graph showing the relationship between percent lactide in the composition as plasticizer and tensile strength.

Figure 2 is a graph showing the relationship between percent

5   lactide in the composition as plasticizer and elastic modulus.

Figure 3 is a graph showing the relationship between percent oligomer in the composition as plasticizer and tensile strength where curve A is for a 90/10 copolymer and curve B is for a 92.5/7.5 copolymer.

10   Figure 4 is a graph showing the relationship between percent oligomer in the composition as plasticizer and the elastic modulus where curve A is for a 90/10 copolymer and curve B is for a 92.5/7.5 copolymer.

Figure 5 illustrates the differential scanning calorimetry (DSC)

15   plot of unannealed 90/10, L-/D,L-lactide copolymer of Example 5B.

Figure 6 illustrates the DSC of the material of Example 5B after remaining at 70 C for 100 minutes.

Figure 7 illustrates the DSC of the material of Example 5B after annealing in 185 F overnight.

20   Figure 8 illustrates the DSC of the material of Example 5B that has been blended with 5 percent calcium lactate.

Figure 9 compares the melt viscosity versus shear rate characteristics of polystyrene and the lactide polymer prepared as in Example 8B.

25   Figure 10 illustrates a DSC for the copolymer of Example 8B.

Figure 11 illustrates a DSC for the L-lactide homopolymer that is added to the copolymer of Example 8B.

Figure 12 illustrates a DSC for the blended composition of Example 23 of the copolymer of Example 8B and a homopolymer of L-lactide.

30   Figure 13 illustrates a differential scanning calorimetry (DSC) plot of 90/10, L-/D,L-lactide copolymer blended with 5 weight percent polystyrene.

- 14 -

DETAILED DESCRIPTION OF THE INVENTION
AND PREFERRED EMBODIMENTS
### First General Embodiment

The environmentally biodegradable compositions disclosed herein

5   are completely degradable to environmentally acceptable and compatible materials. The intermediate products of the degradation: lactic acid and short chain oligomers of lactide or lactic acid are widely distributed naturally occurring substances that are easily metabolized by a wide variety of organisms. Their natural end degradation products

10 are carbon dioxide and water. Contemplated equivalents of these compositions such as those that contain minor amounts of other materials, fillers, or extenders can also be completely environmentally degradable by proper choice of materials. The compositions herein provide environmentally acceptable materials because their physical

15 deterioration and degradation is much more rapid and complete than the conventional nondegradable plastics that they replace. Further, since all or a major portion of the composition will be polylactic acid, and/or a lactic acid derived lactide or oligomer, no residue or only a small portion of more slowly degrading residue will remain. This

20 residue will have a higher surface area than the bulk product and an expected faster degradation rate.

The general application of the invention results in the first and general embodiment of the invention. The homopolymers of D-lactide, L-lactide, D,L-lactide as well as copolymers of D-lactide, L-lactide; D-

25 lactide, D,L-lactide; L-lactide, D,L-lactide; and D-lactide, L-lactide, and D,L-lactide all produce materials useful in the invention when plasticized by lactide monomers, lactic acid, oligomers of lactide, oligomers of lactic acid, and mixtures thereof. The plasticizer may be produced by stopping the reaction before polymerization is completed.

30 Optionally additional plasticizer consisting of lactide monomers (D-lactide, L-lactide, D,L-lactide, or mixtures thereof), lactic acid, oligomers lactide or oligomers of lactic acid, and mixtures thereof can be added to the polymer. The polymer is defined by the formula:
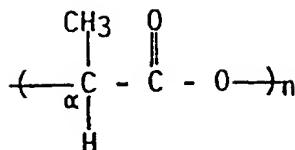
$$\left(-\underset{\underset{H}{\overset{CH_3}{\underset{|}{\alpha C}}}}{}- \overset{\overset{O}{\overset{\|}{}}}{C} - O\right)_n \qquad\qquad I$$

where n is the degree of polymerization (number of repeating units),
5 and is plasticized with a plasticizer derived from incomplete polymer-ization of the monomers used to produce the polymer. The more intimately the plasticizer is integrated with the polymer the better are its characteristics. If desired additional monomer or oligomer can be added to any residual monomer or oligomer remaining in the
10 composition. The oligomers of lactic acid useful for a plasticizer are defined by the formula II, where m is an integer: $2 \leq m < 75$, however, the preferable range is: $2 \leq m \leq 10$.
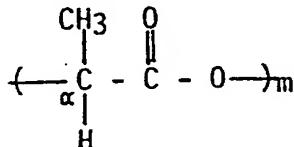
$$\left(-\underset{\underset{H}{\overset{CH_3}{\underset{|}{\alpha C}}}}{}- \overset{\overset{O}{\overset{\|}{}}}{C} - O\right)_m \qquad\qquad II$$

15
The proportions of L-lactide, D-lactide, and D,L-lactide are not critical to obtaining flexible thermoplastics. The parts of L-lactide, D-lactide, and D,L-lactide can vary over a wide, weight-ratio to form a homopolymer or copolymer. The lactide monomers employed in accordance
20 with the invention are available commercially so that neither the monomeric reactant per se nor the method by which it is prepared constitute any portion of the invention.

D-lactide is a dilactone, or cyclic dimer, of D-lactic acid. Similarly, L-lactide is a cyclic dimer of L-lactic acid. Meso D,L-
25 lactide is a cyclic dimer of D- and L-lactic acid. Racemic D,L-lactide comprises a mixture of and L-lactide. When used alone herein, the term "D,L-lactide" is intended to include meso D,L-lactide or racemic D,L-lactide.

One of the methods reported in the literature for preparing a
30 lactide is to dehydrate lactic acid under high vacuum. The product is distilled at a high temperature and low pressure. Lactides and their preparation are discussed by W. H. Carothers, G. L. Dorough and M. J. Johnson (J. Am. Chem. Soc. 54, 761-762 [1932]); J. Gay-Lussac and J. Pelouse (Ann. 7, 43 [1833]); C. A. Bischoff and P. Walden (Chem. Ber.

- 16 -

26, 263 [1903]; Ann. 279, 171 [1984]); and Heinrich Byk (Ger. Pat. 267,826 [1912]); through Chem. Abstr. 8, 554, 2034 [1914]).

The optically active acids can be prepared by direct fermentation of almost any nontoxic carbohydrate product, by-product or waste,
5 utilizing numerous strains of the bacterial genus Lactobacillus, e.g. Lactobacillus delbrueckii, L. salivarius, L. casei, etc. The optically active acids can also be obtained by the resolution of the racemic mixture through the zinc ammonium salt, or the salt with alkaloids, such as morphine. L-lactide is a white powder having a molecular
10 weight of 144. If an impure, commercially-available product is employed in accordance with the present invention, it is preferable to purify it by recrystallization from anhydrous methyl isobutyl ketone. The snow-white crystals of L-lactide melt at 96-98 C.

D,L-lactic acid which is used in the preparation of D,L-lactide is
15 available commercially. The D,L-lactic acid can be prepared syn-thetically by the hydrolysis of lactonitrile (acetaldehyde cyanohydrin) or by direct fermentation of almost any nontoxic carbohydrate product, by-product or waste, utilizing numerous strains of the bacterial genus Lactobacillus. D,L-lactide is a white powder having a molecular weight
20 of 144. If an impure, commercially-available product is employed in accordance with the present invention, I prefer to purify it by recrystallization from anhydrous methyl isobutyl ketone. One such commercially available product comprising a mushy semisolid melting at 90-130 C was recrystallized from methyl isobutyl ketone and
25 decolorized using charcoal. After three such recrystallizations, the product was tumble-dried in vacuo under a nitrogen bleed for 8 to 24 hours at room temperature. The snow white crystals thus obtained comprise a D,L-lactide mixture melting from 115-128 C.

In preparing the compositions in accordance with the invention, it
30 is preferred to carry out the reaction in the liquid phase in a closed, evacuated vessel in the presence of a tin ester of a carboxylic acid containing up to 18 carbon atoms. The compositions however, can also be prepared at atmospheric pressure with the polymerization system blanketed by an inert gas such as, for example, nitrogen. If
35 polymerization is conducted in the presence of oxygen or air, some

- 17 -

discoloration occurs with a resulting decrease in molecular weight and tensile strength. The process can be carried out at temperatures where the polymerization is sluggish in its later stages so as to trap residual monomer in the viscous polymer melt. Preferred temperatures 5 for this purpose are generally between the melting points of pure L-lactide and pure D,L-lactide, or between 95 to 127 C. While in no way wishing to limit the scope of the invention it is presently believed that below about 129 C, the following occurs:

1. The lactide monomer mixture of L- and D,L-lactide monomers
10   melt to form a eutectic mixture, which melts to a mobile fluid that is an intimate solution of one, two, or three monomers.

2. The fluid melt is polymerized by catalyst to form an increas-ingly viscous solution and eventually unreacted monomer is trapped in association with the polymer as a solution, rather
15   than as a distinct heterogeneous phase. The monomer no longer can react since the reaction is extremely diffusion controlled and cannot contact the low concentration of active end-groups of the polymer.

3. The polymerization ceases or slows considerably so that at
20   room temperature the blend of monomer and polymer are a solid solution that imparts plasticization, clarity, and flexibility to the composition.

4. The catalyst deactivates so that subsequent melt-fabrication does not reinitiate the polymerization.

25   5. The plasticized composition is quite stable since the residual monomer is very high boiling, e.g., lactide boiling point is 142 C at 8 torr, and is tightly associated with its open-chain tautomer, polylactide.

Alternatively, the process can be carried out at any temperature 30 between the melting point of the L-lactide and 200 C and lactic acid or lactide is subsequently melt or solvent-blended into the polymer as a further processing step. Temperatures above 200 C are undesirable because of the tendency of the copolymer to be degraded. Increasing the temperature within the range of 95 to 200 C generally increases the 35 speed of the polymerization. Good results are obtained by heating a

- 18 -

mixture of L-lactide and D,L-lactide at a temperature between about
110 C and 160 C.

The catalysts employed in accordance with the invention are tin
esters of carboxylic acids containing up to 18 carbon atoms. Examples
5 of such acids are formic, acetic, propionic, butyric, valeric, caproic,
caprylic, pelargonic, capric, lauric, myristic, palmitic, stearic and
benzoic acids. Good results have been obtained with stannous acetate
and stannous caprylate.

The catalyst is used in normal catalytic amounts. In general, a
10 catalyst concentration in the range of about 0.001 to about 2 percent
by weight, based on the total weight of the L-lactide and D,L-lactide
is suitable. A catalyst concentration in the range of about 0.01 to
about 1.0 percent by weight is preferred. Good results were obtained
when the catalyst concentration is in the range of about 0.02 to about
15 0.5 percent by weight. The exact amount of catalyst in any particular
case depends to a large extent upon the catalyst employed and the
operating variables including time and temperature. The exact
conditions can be easily determined by those skilled in the art.

The reaction time of the polymerization step, per se, is governed
20 by the other reaction variables including the reaction temperature, the
particular catalyst, the amount of catalyst and whether a liquid
vehicle is employed. The reaction time can vary from a matter of
minutes to a period of hours, or days, depending upon the particular
set of conditions which are employed. Heating of the mixture of
25 monomers is continued until the desired level of polymerization is
detected. The level of polymerization can be determined by analysis
for residual monomers. As discussed previously, the reaction
temperature can be chosen to enhance the incorporation of monomer and
provide plasticized compositions coming directly out of the
30 polymerization reactor. The reaction can be halted at such time that
the composition has attained the conversion of monomer to polymer that
is desired to achieve the desired plastization. In the preferred
embodiment of the invention, approximately 2 to 30 percent lactide is
left unreacted, depending on the plasticization to be achieved.

In general it is preferred to conduct the polymerization in the absence of impurities which contain active hydrogen since the presence of such impurities tends to deactivate the catalyst and/or increase the induction time.   It is also preferred to conduct the polymerization
5   under substantially anhydrous conditions.

The copolymers of the invention can be prepared by bulk polymerization, suspension polymerization or solution polymerization.   The polymerization can be carried out in the presence of an inert normally-liquid organic vehicle such as, for example, aromatic hydrocarbons,
10   e.g., benzene, toluene, xylene, ethylbenzene and the like; oxygenated organic compounds such as anisole, the dimethyl and diethyl esters of ethylene glycol; normally-liquid saturated hydrocarbons including open chain, cyclic and alkyl-substituted cyclic saturated hydrocarbons such as hexane, heptane, cyclohexane, alkylcyclohexanes, decahydronaph-
15   thalene and the like.

The polymerization process can be conducted in a batch, semi-continuous, or continuous manner.   In preparing the lactide monomeric reactants and catalyst for subsequent polymerization, they can be admixed in any order according to known polymerization techniques.
20   Thus, the catalyst can be added to either of the monomeric reactants. Thereafter, the catalyst-containing monomer can be admixed with the other monomer.   In the alternative, the monomeric reactants can be admixed with each other.   The catalyst can then be added to the reactant mixture.   If desired, the catalyst can be dissolved or
25   suspended in an inert normally-liquid organic vehicle.   If desired, the monomeric reactants either as a solution or a suspension in an inert organic vehicle can be added to the catalyst, catalyst solution or catalyst suspension.   Still further, the catalyst and the monomeric reactants can be added to a reaction vessel simultaneously.   The
30   reaction vessel can be equipped with a conventional heat exchanger and/or a mixing device.   The reaction vessel can be any equipment normally employed in the art of making polymers.   One suitable vessel, for example, is a stainless steel vessel.

The environmentally biodegradable compositions produced in
35   accordance with the present invention depending upon the L-lactide, D-

lactide, meso D,L-lactide ratios, find utility in articles of manu-
facture, such as films, fibers, molding and laminates, which are
prepared by conventional fabricating methods. These articles of
manufacture are contemplated for nonmedical uses i.e. outside the body
5 where they can substitute for the common environmentally nondegradable
plastics.

Filaments, for example, are formed by melt-extruding the copolymer
through a spinneret. Films are formed by casting solutions of the
biodegradable compositions and then removing the solvent, by pressing
10 solid biodegradable compositions in a hydraulic press having heated
platens, or by extrusion through a die.

Various techniques including slow cooling and rapid cooling can be
employed in preparing moldings from the copolymers of the invention.

Contemplated equivalents of the compositions of the invention are
15 those that contain minor amounts of other materials. The copolymers
produced in accordance with the present invention can be modified, if
desired, by the addition of a cross-linking agent, other plasticizers,
a coloring agent, a filler and the like.

Cross-linking can be effected by compounding the compositions with
20 free-radical initiators such as cumene hydroperoxide and then molding
at elevated temperatures. This can improve heat-and solvent-resist-
ance. Curing can also be effected by compounding the copolymers with
multifunctional compounds such as polyhydric alcohols and molding, or
thermoforming under heat and vacuum. Graft-extruder reactions to
25 effect curing of the polyesters is an obvious method of cross-linking
and chain-extending the copolymers.

In preparing moldings, a filler can be incorporated in the
compositions prior to curing. A filler has the function of modifying
the properties of a molding, including hardness, strength, temperature
30 resistance, etc. Known filler materials include aluminum powder,
powdered calcium carbonate, silica, kaolinite (clay), magnesium
silicate and the like. Of particular advantage is starch, which blends
well with the compositions to obtain a blend which is totally
environmentally biodegradable. Other property modifications can be

effected by melt blending the compositions with other polymers and copolymers of the lactides, glycolides, and caprolactone.

The compositions prepared according to the present invention can be used in producing reinforced laminates according to known
5 procedures. In general, laminates are made from a fibrous mat or by assembling a multiplicity of sheets of material to form a matrix which is consolidated into a unitary structure by flowing molten precursor or composition through the fibrous material and curing it while in a mold or hydraulic press to form the polymer. Fibers which are used in
10 forming the matrix include natural and synthetic fibers such as cellulose derived from wood, cotton, linen, hemp, and the like, glass, nylon, cellulose acetate and the like.

The compositions of the invention and their preparation are further illustrated by the following specific examples.

15 Example 1
                    80/20, L-lactide/racemic D,L-lactide
160 grams of L-lactide and 40 grams of racemic D,L-lactide, both of high purity (Purac, Inc., triply recrystallized), were charged into a 500 ml, round-bottom flask and purged with dry nitrogen overnight.
20 10 ml of stannous octoate is dissolved in 60 ml of anhydrous toluene, and 10 ml of the solvent is distilled to a Dean-Stark trap to effect dryness of this catalyst solution by azeotropic distillation. From the 10 ml of stannous octoate in 50 ml of dry toluene a 0.20 ml portion is removed with a syringe and injected into the lactides in the reaction
25 flask. The nitrogen purge is continuous via a syringe needle connec- tion that enters the reaction flask through a rubber septum and vents via a piece of tubing that connects to a bubbler. The nitrogen flow is maintained at 1-3 bubbles per second. The flask was heated in an oil bath maintained at 123-127 C. During the first part of the heating the
30 lactides melt and are mixed thoroughly by swirling. Thereafter, the products become quite viscous. After 20 hours of heating, the flask and the colorless, transparent products are removed from the heating bath, cooled, the flask broken, and shocked with liquid nitrogen to remove glass from the product. The copolymer was molded in a heated

- 22 -

hydraulic press.   Compression molding to 5 to 10 mil thick films was possible at 20,000 lb pressure, at 170 C, in a time period of 2 minutes.   The films were evaluated for their tensile properties on a Instron tester, and the results are listed in Table 1.   Samples 1/8

5   inch thick were also molded for impact strength testing.   A thermal gravimetric analysis (TGA) of the product was performed, noting the weight loss upon heating the sample to 150 C in 4 minutes and holding the temperature at 150 C for 60 minutes.   The weight loss of the sample was 19.5 percent and nearly complete in 60 minutes.   The weight loss is

10   attributed to loss of lactide monomer.   Results of differential scanning calorimetry (DSC) reveal that the composition has an endotherm beginning about 110 C, becoming more pronounced as the temperature increases to 200 C.   No melting point was observed.   Specimens were annealed at 185 F overnight and reexamined.   They remained transparent,

15   colorless and pliable.   Samples of the copolymer could be remolded 6 times without any discoloration or obvious loss of strength.   Thin films were clear, transparent, colorless, and quite flexible, despite the repeated molding.

TABLE 1.   PROPERTIES OF COPOLYMERS[a] OF L-LACTIDE AND
D,L-LACTIDE WHEN PLASTICIZED BY LACTIDE

Example No.	1	2	3
Film thickness, mil	8	8	10
Tensile strength, 1000 psi, ASTM D638	3.9	1.7	7.9
Elongation, percent	28	806	3.5
100 percent modulus, 1000 psi	0.74	--	--
200 percent modulus, 1000 psi	1.20	--	--
Tangent modulus, 1000 psi	36.6	--	289
Izod impact strength, ft-lb/in.[b]	0.63	--	0.4
M_w, 1000's	540	281	341
M_n, 1000's	270	118	97.5
Residual lactide,[c] percent	19.5	27.8	2.7

(a)   80/20, weight ratio, of L-/racemic D,L-lactide.
(b)   1/8 inch, notched samples.
(c)   By isothermal TGA weight loss at 150 C.

Example 2

In a 3-liter, round-bottom flask was charged 1.84 Kg of L-lactide, 0.46 Kg of racemic D,L-lactide and 2.3 ml of the stannous octoate solution, similar to Example 1. The mixture was purged with argon for 3 hours, then heated isothermally in a 125 C oil bath. The mixture melts, was mixed thoroughly by swirling, and forms a homogeneous, transparent, colorless fluid whose viscosity increases substantially after several hours. After 64 hours the flask was removed from the heating bath, cooled, and the glass removed from the clear, transparent, solid product. The rubbery composition was guillotined

- 24 -

into slices and ground to 1/8 inch, or smaller, size in a grinder with dry ice. The grind was dried in an air circulating oven at 100 F for several hours, then vacuum dried overnight at ambient temperature. Compression-molded films were prepared as described in Example 1 and

5 the films were examined for their tensile properties and weight loss by TGA as shown in Table 1.

Example 3

In a 250-ml, round bottom flask was placed 79.98 g of L-lactide, 20.04 g of racemic D,L-lactide, and 0.20 ml of stannous octoate

10 solution, similar to Example 1. The flask was swept by nitrogen through inlets and outlets and heated in a 125 C oil bath. The mixture melted to a colorless and fluid liquid that was thoroughly mixed by swirling the flask. After 2 hours, the oil bath temperature was increased to 147 C, and after 14 hours total heating time, the

15 temperature was decreased to 131 C. Total heating time was 18 hours. The product is transparent, colorless, and glassy. It was evaluated, similar to the preceding examples and the results are recorded in Table 1.

Examples 1 to 3 reveal the effect of reaction temperature on the

20 properties of the copolymers as occasioned by the resulting composition.

Example 4

Films of the copolymers of Examples 1 and 3 were immersed in water for several months. After 3 weeks, the copolymer of Example 1 became

25 hazy while that of Example 3 remained clear for approximately 2 months; after 3 months the film of Example 3 became noticeably hazy and the film of Example 1 is white and opaque. The water that had been in contact with the film of Example 1 tastes acidic while that of Example 3 is tasteless.

30 Inspection of the data of Table 1 reveals that the copolymer of Example 1 is an environmentally biodegradable replacement for polyethylene. Those skilled in the art will recognize that the physical properties of the copolymer are an excellent combination

useful for many packaging applications. Its tensile strength and initial tangent modulus compare favorably with polyethylene compositions used, for example, in plastic trash bags, general film wrap, plastic shopping bags, sandwich wrap, six pack yokes and the
5   like. The shape of the stress-strain curves are approximately the same for both the copolymer and that for a linear low density polyethylene composition commonly used in trash bag compositions. A comparison of properties are shown in Table 2.

TABLE 2.   COMPARISON OF POLYETHYLENE TO POLYLACTIC ACID POLYMERS

10

Property	LDPE-[a] NA 272	LLDPE[b]	Lactide Copolymer[c]
Tensile strength, 1000 psi, ASTM Standard C	2.18	2.9	3.90
Elongation, %	261	500	280
Tangent modulus, 1000 psi	54.9	51.0	36.6
100% modulus, 1000 psi	1.77	--	0.74
200% modulus	1.82	--	1.20
HDT,[d] 264 psi, F	95	99	122

25   (a)   Linear low density polyethylene, 5-10 mil, 2-in./min., our experiments.
     (b)   Linear low density polyethylene, data from computer file.
     (c)   Copolymer of L-lactide/racemic D,L-lactide, Example 1.
     (d)   Heat deflection temperature.

30   The lactide polymerization can be stopped at incomplete monomer-to-polymer conversion in a controllable fashion. This is illustrated in Examples 1 and 2. The lactide monomer binds very intimately with polymers of lactides. Alternatively, the compositions can be derived

- 26 -

by mixing of lactide with preformed polymer. In that case, the lactide added can be the same or different with respect to stereochemistry, i.e., L-, D-, or D,L-lactide to that used to make the polymer.

The compounding can be accomplished by blending the molten polymer
5   with lactide monomer in conventional processing equipment such as a mill roll or a twin screw compounder. The normally stiff, glassy, lactide polymers are flexibilized by the lactide and remain transparent, colorless, and very nearly odorless. The lactide is not very fugitive, requiring heating, and a nitrogen sweep, typically, 170-
10   200 C for 20-60 minutes to remove the lactide in a gravimetric analysis. Neither is the lactide visible in films under an optical microscope. The lactide domains are submicron in size. This flexibilizing of the polylactic acid suggests its use as a environmentally biodegradable replacement for polyolefin, disposable,
15   packaging films.

Examples 5-16

A series of experiments were performed in which copolymers of L- and racemic D,L-lactide were prepared, melt blended with variable amounts of lactide, and the physical properties of the blends evaluated
20   as a function of the lactide composition. Monomer lactide content was assayed by a previously developed isothermal, thermogravimetric analysis (TGA). The lactide contents were measured before and after compounding and molding into films.

It was observed that open roll, 2 roll, milling tended to
25   volatilize the lactide at temperatures required for the very high, molecular weight lactide copolymers. These losses could be minimized by masterbatching or by using lower molecular weight lactide copolymers (and their lower attendant mixing temperatures). A better mixing and blending method was a conventional, twin screw extruder, which
30   minimized volatile losses. Some results are shown in Table 3. The blends of polylactide and lactide plasticizer are quite pliable, becoming increasingly so with increasing lactide content. They are colorless and transparent. Only a very faint (pleasant) odor of lactide is detectable and no discernable taste of lactide was

noticeable. The Table 3 plasticized film samples were tear resistant, easily foldable, and can be punctured without shattering or tearing. They stiffen somewhat when placed in a cooler (5 C, 40 F), but remain flexible and creasible without breaking. These films noticeably soften

5 in the hand, indicating a glass transition temperature below 37 C. When the lactide content is less than 20 percent, the films will have a rattle typical of a polyolefin film. At greater lactide contents the films have the drape and "warm" feel of a PVC.

As shown in Table 3, the elastic moduli (initial tangent moduli)

10 can be relatively high, similar to a linear low density polyethylene (LLDPE). This is an indication of potential form stability. Lower moduli and tensile strengths are similar to low density polyethylene (LDPE). Physical properties, as a function of lactide content, were plotted as shown in Figures 1 and 2. Referring to Table 3, at

15 approximately 17-20 percent lactide content, the tensile properties are similar to polyethylenes used in trash bags and shopping bags.

At lower lactide contents, the blends have a similarity to polypropylene. Some data can be compared in Table 3. Table 4 defines the conventional plastics used in the comparisons.

TABLE 3. TENSILE PROPERTY COMPARISONS OF PLASTICIZED PLA(a)

Example No.	Composition	Lactide %, TGA	Elastic Modulus, 1000 psi	1% Secant Modulus, 1000 psi	Yield Strength, 1000 psi	Strain at Yield, %	Break Strength, 1000 psi	Strain at Break, %
5	90/10, L-/D,L- Lactide Copolymer	1.3	289	291	0	0	7.5	3
6	"	17.3	119	119	2.23	4	2.29	288
7	"	19.2	95.5	90.3	1.97	5	4.24	536
8	"	19.6	88.7	88.7	1.72	4	2.12	288
9	"	20.5	50.3	50.3	1.21	5	2.16	338
10	"	25.5	33.7	22.9	0.32	4	2.44	546

(a) ASTM 882; all samples were compression molded 5-10 mil films except Examples 13 and 14; strain rate 1.0 in/in min for all, D,L-lactide is racemic.

(CONTINUED)

TABLE 3.   TENSILE PROPERTY COMPARISONS OF PLASTICIZED PLA(a)

Example No.	Composition	Lactide, %,TGA	Elastic Modulus, 1000 psi	1% Secant Modulus, 1000 psi	Yield Strength, 1000 psi	Strain at Yield, %	Break Strength, 1000 psi	Strain at Break, %
11	LDPE(b)	--	41.3	40.6	1.51	17	1.60	365
12	LLDPE(c)	--	44.4	42.7	1.66	16	1.66	599
13	Biaxially(d) oriented PE	--	38.9	41.1	1.69	16	4.78	838
14	"(e)	--	35.6	38.5	1.68	16	5.20	940
15	HDPE(f)	--	127.8	120.9	3.48	9	1.95	216
16	pp(g)	--	174	174	5.08	5	7.34	6

(b)   USI low density polyethylene (petrothene No. 213).
(c)   Exxon linear low density polyethylene (LLPE 6202,57).
(d)   Machine direction.
(e)   Cross machine direction.
(f)   Phillips high density polyethylene (HMN 5060).
(g)   Chisso polypropylene (XF 1932, melt index 0.52).

- 30 -

TABLE 4. MANUFACTURERS' DATA

Supplier	Trade Name and/or Grade	Density, gm/cu cm	Recommended Melt Temperature, F	Tensile Strength at Yield	Elastic Modulus in Flexure, 35 psi	Melt Index gm/10 min
LDPE (USI)	Petrothene No. 213	0.924	360-550	1820	0.37	8.0
LLDPE (Exxon)	6202.57	0.926	425	1700	0.53	12.0
HDPE (Phillips)	HMN 5060	0.950	425-525	3600	1.75	6.0
80% LLDPE (Exxon) 20% HDPE (Processing oil)	LPX 86 (Octene base)	0.927	260	--	--	0.8
Polypropylene (PP-Chisso)	XF1932	0.91	450-500	5872	3.05	0.52
Polystyrene (Amoco)	RI	1.05	400	7900	4.50	1.8

Table 3 reveals some data for lactide and polylactide mixtures. The results do not differ remarkably from similar compositions of Examples 1 and 2, prepared by other means. However, those skilled in the art will recognize that the precise physical properties will vary
5 somewhat depending on the intimacy of the mixture, the tensile testing conditions, and the fabrication technique for preparing the films. Comparisons from Table 3 reveal that the lactide-polymer mixtures have a broad range of controllable compositions that mimic many conventional, nondegradable plastic types.

10 Example 17

An oligomeric polylactic acid (OPLA) was prepared for mixing with polylactides as follows. An 88 percent solution of L-lactic acid (956 g) was charged to a 3-neck flask (1 liter) fitted with a mechanical stirrer and a pot thermometer. The reaction mixture was concentrated
15 under a nitrogen purge at 150-190 C at 200 mm Hg for 1 hour until the theoretical water of dilution was removed. No catalyst was used except for lactic acid and its oligomers. This temperature and vacuum were maintained and distillation continued for 2 hours until 73 percent of the theoretical water of dehydration was removed.

20 The total time required was 3 hours. At this time the reaction was stopped. The water samples and the pot oligomer were titrated with 0.5N NaOH. Some lactic acid, 26.2 g, was found in the water distillate. The pot oligomer (OPLA) was also refluxed with excess 0.5N NaOH, then back titrated with standard H_2SO_4. The data are recorded
25 in Table 5. The OPLA flows well when hot, and shows some cold flow. It has a degree of polymerization of 3.4. It was used in Example 20 where it was melt blended with the polymer of Example 19.

- 32 -

TABLE 5.   CHARACTERIZATION OF OPLA OF EXAMPLE 1

Percent Dehydrated, Theoretical	Titratable Acid, percent	Titratable Ester, percent	Total Expressed as Lactic Acid percent	Degree of Polymerization
58	34.4	82.4	116.8	3.4

Example 18

The procedure of Example 17 was repeated except the distillation was conducted more slowly. After 8 hours of heating during which the temperature was slowly advanced from 63 to 175 C at 200 mm Hg, a sample of the pot was titrated to reveal 62.2 percent of theoretical water removal. Titration revealed a degree of polymerization of 4.3. The molecular weight of the OPLA was further advanced over 2 hours by heating at 179 C and using a vacuum pump. The OPLA was no longer soluble in 0.1N NaOH, was water white, and would cold flow. This material is a second example of an OPLA preparation with somewhat higher degree of polymerization as compared to Example 1. It was mixed with polylactide in Examples 22 and 25. It is estimated that the degree of polymerization was about 6-10.

Example 19

A polymer of lactide was prepared by methods similar to Example 3. A 90/10, weight percent L-/racemic D,L-lactide copolymer was melt polymerized using 0.02 parts per hundred, anhydrous stannous octoate catalyst. In a similar manner a 100 percent L-lactide homopolymer (L-PLA) was prepared. The copolymer was melt blended with the homopolymer at 350 F in a twin-screw extruder at a weight ratio of 90/10, copolymer/homopolymer. Gel permeation chromatography (GPC) of the blend reveals a weight-average molecular weight (M_w) of 182,000 and a

- 33 -

number-average molecular weight (M_n) of 83,000. Residual lactide monomer by thermogravimetric analysis (TGA) was 1.7 weight percent. This blend was mixed with the oligomeric polylactic acid of (OPLA) of Example 17 to provide Example 20. The tensile properties are listed in
5   Table 6.

Example 20

The polymer of Example 19 was melt blended with the OPLA of Example 17 on an open, 2-roll, mill for 20 minutes at 325 F. The mix was compression molded into films and tested as shown in Table 6. The
10   GPC molecular weights were smooth, monomodal distributions (M_w/M_n = 2.6) with M_w = 192,000 and M_n = 73,000.

TABLE 6.   PROPERTIES OF MELT BLENDS OF 90/10 POLYLACTIDES AND OLIGOMERIC POLYLACTIC ACID

Example Number	Composition, wt.% Polymer	Oligomer	Lactide, % TGA	Elastic Modulus, 1000 psi (a)	Break Strength, psi (a)	Strain at Break, % (a)	Tg, C (b)
19	100(c)	0	1.7	298	7500	3	55
20	91(c)	9(d)	1.8	275	6113	2	--
21	100(e)	0	1.6	308	7478	3	58
22	70(e)	30(f)	0.4	254	5052	3	42
23	60(e)	40(f)	0.0	202	3311	2	38
24	50(e)	50(f)	0.0	106	2334	25	35
25	40(e)	60(f)	0.0	36	1180	129	35

(a) ASTM 882; 5-10 mil, compression-molded films; strain rate 1.0 in./in./min.
(b) Glass transition temperature by differential scanning calorimetry.
(c) A blend of 90% of a 90/10, L-/D, L-lactide*copolymer with 10% poly(L-lactide), Example 19.
(d) Oligomeric PLA of Example 17.
(e) A blend of 80% of a 90/10, L-/D,L-lactide*copolymer with 20% poly(L-lactide).
(f) Oligomeric PLA of Example 18.

* racemic

Example 21-25

The copolymer of Example 19 was melt blended with 20 percent of the L-PLA described in Example 19. The blend is listed as Example 21 in Table 6, where its analyses and tensile properties are listed.
5 Example 21 was, in turn, melt blended with various amounts of the OPLA of Example 18 and these were tested as before and listed in Table 6, Examples 22 to 25. Table 7 lists the GPC molecular weights of these compositions. The tensile strengths and moduli are compared to the weight percentages of OPLA in Figures 3 and 4 (Lower Curves).

TABLE 7.   MOLECULAR WEIGHTS AND GLASS TRANSITION TEMPERATURES
OF 90/10 POLYLACTIDES AND OLIGOMERIC POLYLACTIC ACID

Example Number	Composition, wt % Copolymer	Oligomer	Res.[a] Mon., %	GPC x 10^{-3}[b] M_n	M_w	M_z	M_w/M_n	Tg,[c] C
21	100[d]	0	1.6	76	175	410	2.3	58
22	70[e]	30[f]	0.4	67[g]	136	299	2.0	42
23	60[e]	40[f]	0.0	61[g]	112	211	1.8	38
24	50[e]	50[f]	0.0	62[g]	114	223	1.8	35
25	40[e]	60[f]	0.0	69[g]	120	207	1.7	35

(a)   Residual monomer by TGA.
(b)   Molecular weight by GPC.
(c)   Glass transition temperature by DSC.
(d)   A blend of 90% of 90/10, L-/D,L-lactide copolymer with 10% L-Pla.
(e)   Example 21.
(f)   Example 18.
(g)   After blending; melt-blending on an open mill roll at 325 F.

All D,L-lactide is racemic.

Examples 26-30

A second series of copolymers was blended with the OPLA. A 92.5/7.5, L-/D, L-lactide copolymer was prepared by methods similar to Examples 19 and 21. This is Example 26 of Tables 8 and 9. It was melt
5 blended with the OPLA of Example 18 on an open, 2-roll mill at 325 F for approximately 20 minutes. The blends were compression molded into 3-5 mil thick films and their tensile properties and GPC molecular weights measured. The properties are recorded in Tables 8 and 9, and plotted in Figures 3 and 4. The second series of blends revealed
10 significantly higher values for the tensile properties although the molecular weights were lower. This may be due to lower residual lactide monomer and/or the change in high polymer composition. All of the OPLA polylactide blends could be easily molded into tack free, transparent films.

TABLE 8. PROPERTIES OF MELT BLENDS OF 92.5/7.5 POLYLACTIDES AND
          OLIGOMERIC POLYLACTIC ACID

Example Number	Composition, wt.% Polymer (c)	Oligomer (d)	Lactide, %, TGA	Elastic Modulus, 1000 psi, (a)	Break Strength, psi (a)	Strain at Break, % (a)	Tg(b) C
26	100	0	0.2	338	10,527	4	61
27	80	20	0.3	346	9,144	4	52
28	70	30	0.2	346	5,675	2	46
29	60	40	0.6	249	5,617	3	36
30	50	50	1.5	112	1,984	119	36

(a) ASTM 882; 3-5 mil compression-molded films; strain rate 1.0 in./in./min.
(b) Glass transition temperature by differential scanning calorimetry.
(c) 92.5/7.5, L-/D,L-lactide copolymer.
(d) Example 18.

All D,L-lactide is racemic.

TABLE 9. MOLECULAR WEIGHTS OF 9.25/7.5,
L-/RACEMIC D,L-LACTIDE COPOLYMERS

Example No.	% OPLA	GPC x 10^{-3} [a] M_n	M_w	M_z	M_w/M_n
26	0	63	124	228	1.95
27	20	60	108	189	1.81
28	30	48	80	125	1.66
29	40	59	96	151	1.65
30	50	56	92	141	1.64

(a) GPC

Examples 31 and 32

Film specimens with, and without plasticizer were exposed to seawater at Daytona, Florida from March through May. The pH of the water varied from 7.3 to 7.6 and the salinity from 33.2 to 38.4 ppt. The water gradually warmed in the test from 15 to 27 C. The specimens were cut into strips and tensile tested before, and after, periodic intervals in the seawater. The results are shown in Table 10. All of the samples showed whitening and physical degradation, which became progressive with time. Without plasticizer the samples showed whitening and degradation after six weeks in the seawater. The OPLA polylactide blend degraded faster, revealing clear evidence of degradation after 3 weeks. The incorporation of 20 percent lactide provoked immediate whitening and obvious degradation after one week of exposure.

TABLE 10. PHYSICAL PROPERTIES AFTER SEAWATER EXPOSURE

Example Number	Composition	Seawater Exposure Weeks	Tensile Properties, 1000 psi[a]				Strain, %	
			Elastic Modulus	1% Secant Modulus	Yield Strength	Break Strength	Yield	Break
31	90/10 copolymer 5% L-PLA	0	305	292	--	7.6	--	4.7
		3(b)	315	301	--	7.1	--	3.1
		6(c)	317	317	--	7.3	--	3.0
		9(d)	228	230	--	6.2	--	3.0
		12(e)	355	343	--	3.9	--	1.0
20	90/10 copolymer with 10% oligomer	0	275	275	--	6.1	--	2.0
		3(b)	291	281	--	6.8	--	2.9
		6(c)	246	246	--	3.9	--	2.0
		9(d)	211	105	2.2	1.4	3	2.0
		12(e)	103	103	--	1.7	--	1.0
32	90/10 copolymer with 1% fumaric acid	0	300	298	--	7.0	--	3.0
		3(b)	292	291	--	6.5	--	2.5
		6(c)	318	318	--	6.9	--	2.0
		9(d)	226	223	--	6.1	--	3.0
		12(e)	70	122	--	0.8	--	1.7
9	92.5/7.5 co-polymer with 20% lactide	1(e)	- - - - - - - Too brittle to test - - - - - -					

(a) 0.5 x 5 in. strips of film, 12-17 mil; strain rate 1 in./in./min.
(b) 15-21 C, saline seawater, regularly exchanged.
(c) 20-22 C, saline seawater, regularly exchanged.
(d) 22-23 C, saline seawater, regularly exchanged.
(e) 22-27 C, saline seawater, regularly exchanged.

The above examples establish that an all lactic acid composition can be a pliable thermoplastic useful for flexible, plastic containers. By way of comparison, nonplasticized homopoly (L-lactide) is a highly crystalline polymer with a tensile strength of about 7000 psi with an
5   elongation of 1 percent and an initial modulus of 500,000 psi. It is very brittle, opaque, and crazes easily. It is not a well behaved thermoplastic, nor is it transparent. Poly (racemic D,L-lactide) is an amorphous, glassy, polymer with a glass transition temperature of approximately 50 C, a tensile strength of about 6300 psi, an elongation
10   of approximately 12 percent, and an initial modulus of 160,000 psi. It is also very brittle although transparent. In stark contrast, a polymer of L-lactide/racemic D,L-lactide copolymer that is plasticized with lactide monomer is remarkably different. For example, the plasticized polymers can have a tensile strength of approximately 3900
15   psi, an elongation of 431 percent, and an initial modulus of 56,000 psi. The plasticized polymer is clear and colorless and the blend must be heated to above 100 C to remove the plasticizer.

     Although theory would predict a more amorphous structure as a result of plasticization, what is surprising is the pliable, transpar-
20   ent, stable compositions that can arise, and, secondly, the nearly exact fit of properties needed for certain packaging applications, such as polyethylene. This invention comes at a time when there is a need for such initial properties in a material that is slowly environmentally biodegradable since it could alleviate plastic
25   pollution problems.

     It will be apparent to those skilled in the art that extremely intimate blends of high polymers and plasticizers are a rarity. Plasticization allows a wide latitude in the initial physical properties and the time for environmental biodegradation.

30   The amount of plasticizer in the polymer depends on the compositional characteristics desired. If lactide is used as plasticizer the range is preferably 5 to 40 weight percent whereas if only oligomers of lactide or lactic acid are used the range may be from 2 to 60 weight percent. Surprisingly, oligomer may be added at up to 30 weight

- 42 -

percent without substantially affecting the tensile strength or modulus. See Figures 3 and 4. Addition of 30 to 60 weight percent oligomers produces significant plasticization and attenuation of physical properties. This adds great economy to the composition since
5 oligomeric lactic acid is cheaper than high polymer lactic acid. Oligomer may be prepared from lactic acid or any lactide. It is important to note that the oligomer of lactic acid normally contains significant amounts of lactic acid unless removed. This is an important consideration in tailoring compositions having specific
10 properties. Those skilled in the art and knowing the teachings of this invention will be able to select reaction conditions to obtain appropriate chain lengths for the polymer, and the proportions of polymer and plasticizer so as to obtain fabricated compositions having physical properties similar to commonly used packaging thermoplastics
15 and yet degrade comparatively rapidly. For example, higher amounts of plasticizer result in polymers having increased flexibility and increasingly tough physical properties, however, an increasing degradation rate will also be obtained. Further, shorter chain lengths for the polymer will require less plasticizer to obtain the same
20 properties as with longer lengths.

Further provided by the first embodiment of the invention is a process for producing a environmentally biodegradable composition that is a plasticized polymer of polylactic acid having the formula (I). The process comprises preparing one or more lactide monomers and
25 catalyst; polymerizing the monomers to form a polymer at a temperature sufficiently low to allow the polymerization reaction to be stopped prior to complete polymerization; monitoring the level of monomer to determine the amount of remaining monomer; and stopping the reaction prior to complete polymerization at a determined amount of monomer so
30 that unreacted monomer of a predetermined amount is trapped in association with the polymer. The lactide monomers of the process are selected from the group consisting of D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof. Optionally one may incorporate additional plasticizer into the polymer whereby the
35 plasticizer is further selected from the group consisting of L-lactide,

D-lactide, racemic D,L-lactide, meso D,L-lactide, lactic acid, oligomers of lactic acid, oligomers of lactide, and mixtures thereof. Preferably polymerization of the monomers is at a temperature less than 129 C. Further processing of the plasticized polymer into a final

5   product is preferably at a temperature sufficiently low to retain the plasticizer in the polymer. This temperature may be above 129 C. If additional monomer and/or oligomer are added the retention of monomer is of course not as critical.

Further provided by the first embodiment of the invention is a

10   process for producing a polymer of formula I comprising preparing one or more lactide monomers and catalyst; polymerizing the monomers to form a polymer; and incorporating plasticizer in a separate step into the polymer whereby the plasticizer is selected from the group consisting of D-lactide, L-lactide, D,L-lactide, oligomers of lactic

15   acid, and mixtures thereof.

The compositions of the invention should have a tensile strength of 300 to 20,000 psi, an elongation to failure of 50 to 1,000 percent and a tangent modulus of 20,000 to 250,000 psi. Preferably for a polyolefin replacement the compositions have a tensile strength of at

20   least 3000 psi, an elongation to failure of at least 250 percent, and a tangent modulus of at least 50,000 psi.

The homopolymers and copolymers of the present invention are insoluble in water but upon constant contact with water are slowly degradable. However, degradation is fast when compared to polyolefin

25   compositions that are replaced by the invention. Thus, throwaway objects made from the polymers are environmentally attractive in that they slowly degrade to harmless substances. If objects made from polymers of the invention are incinerated, they burn with a clean, blue flame.

30   Yet further provided by the first embodiment of the invention is a method for replacing a thermoplastic composition with the biodegradable composition of the invention where the thermoplastic composition comprises first orientable polymer units, by replacing the first polymer units with a second orientable polymer having an

35   unoriented tensile strength of 300 to 20,000 psi, an elongation to

- 44 -

failure of 50 to 1,000 percent, and a tangent modulus of 20,000 to 250,000 psi; wherein the second polymer comprises polylactic acid units of the structure in formula I, wherein n is the number of repeating units and n is an integer, $150 \leq n \leq 20,000$ and is plasticized with a
5 plasticizer selected from the group consisting of lactide, oligomers of lactic acid, oligomers of lactide and mixtures thereof. The method is useful for polyolefin compositions and particularly polyethylene and polypropylene as well as polyvinyl chlorides and polyethylene terephthalate. In addition to the above list the method is useful for
10 replacement of polymers of styrene, vinyl acetate, alkyl methacrylate, alkyl acrylate. It is understood that copolymers made from mixtures of the monomers in the listed group and physical mixtures of the polymers and copolymers of the above group are likewise replaceable.

15 Second General Embodiment
     The environmentally biodegradable compositions disclosed as a second embodiment herein are completely degradable to environmentally acceptable and compatible materials. The intermediate products of the degradation: lactic acid is a widely distributed naturally occurring
20 substance that is easily metabolized by a wide variety of organisms. Its natural end degradation products are carbon dioxide and water. Contemplated equivalents of these compositions such as those that contain minor amounts of other materials, fillers, or extenders can also be completely environmentally degradable by proper choice of
25 materials. The compositions herein provide environmentally acceptable materials because their physical deterioration and degradation is much more rapid and complete than the conventional nondegradable plastics that they replace. Further, since all or a major portion of the composition will be polylactic acid, and/or a lactic acid derived
30 lactide or oligomer, no residue or only a small portion of more slowly degrading residue will remain. This residue will have a higher surface area than the bulk product and an expected faster degradation rate.
     The preferred composition of the present invention comprises polymerized lactic acid units with the repeating unit of formula I, wherein
35 n is an integer with a value between 75 and 10,000 and the alpha carbon

is a random mixture of D and L (or R and S) with a preponderance of one of the pure enantiomeres. When n is low, the polylactic acid, PLA, is easily processible, but is considerably weaker than when n is larger. When n is quite large, e.g., 7000 or greater, the PLA is quite strong

5 but difficult to injection mold. Preferably n is approximately 500 to 3000 for the best balance of melt-processibility and end-use physical properties. The monomers are selected in L (or D)/D,L-ratios of polymerized lactic acid or their cyclic dimer, lactide, as further discussed below. Both lactic acid and lactide achieve the repeating

10 PLA unit, shown above, but lactide is preferred since it more easily obtains the higher molecular weights necessary for good physical properties. Since lactide, which has the structure:

15

$$O = C \underset{H-C-O}{\overset{O-C-H}{\diagup}} C = O$$

$$\underset{CH_3}{\overset{CH_3}{|}}$$
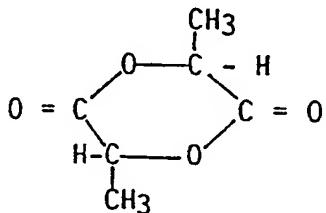
has two alpha carbons which are assymetric, there are three types of lactide, viz., D,D- (or D-); L, L- (or L-); and meso D,L-lactide.

20   D-lactide is a dilactide, or cyclic dimer, of D-lactic acid. Similarly, L-lactide is a cyclic dimer of L-lactic acid. Meso D,L-lactide is a cyclic dimer of D- and L-lactic acid. Racemic D,L-lactide comprises a 50/50 mixture of D-, and L-lactide. When used alone herein, the term "D,L-lactide" is intended to include meso D,L-lactide

25 or racemic D,L lactide. The term dispersed as used herein means the material is homogeneously and intimately mixed with the polymer.
       Pure L-PLA has poor processing characteristics, easily crazes and becomes opaque. Pure D,L-PLA processes easily but is not sufficiently rigid to be an adequate OPS offset. The copolymer ratio of between

30 85/15 to 95/5, and preferably 90/10, L-lactide/D,L-lactide is a preferred embodiment of the invention. At higher ratios than 95/5, the copolymer is difficult to thermoform without crazing and easily becomes opaque at room temperature. At lower ratios than 85/15, the lactide copolymers exhibit lower than desirable moduli for OPS offsets. In

between these limits the copolymers are quenched from the melt in typical manufacturing/processing equipment of plastics technology to achieve films and moldings which are clear, colorless, and extremely rigid. Their properties as formed, above, are closely matched to those
5 properties of an OPS.

Another advantage of this invention is that the all-lactic acid copolymer can utilize inexpensive feedstocks. Corn syrup via starch and corn can be fermented to either L- or racemic D,L-lactic acid, depending on the microorganism. Racemic D,L-lactic acid is cheaply
10 obtainable via ethylene which can be oxidized to acetaldehyde, which is reacted with hydrogen cyanide to form lactonitrile, which is hydrolyzed to racemic D,L-lactic acid. Lactide is simply obtained by distillation of lactic acid. No change of the stereochemistry of the asymmetric carbon occurs in transforming lactic acid to lactide by ordinary
15 distillation/condensation methods.

While the reaction of L-lactide and D,L-lactide is discussed herein, it is to be understood that the reactions specifying L-lactide may also use D-lactide. Thus the reaction of D-lactide and D,L-lactide according to the method described herein will give an equivalent
20 product; the only difference being that it rotates light in a different direction.

The copolymers of the present invention are preferably formed by heating the mixture of monomers to form a homogeneous melt and adding a catalyst to cause the lactides to undergo a ring-opening polymeriza-
25 tion. The polymerization is preferably carried out in an inert, anhydrous, atmosphere, such as nitrogen or argon, or in a vacuum. Suitable catalysts include divalent metal oxides and organo-metallic compounds such as stannous octoate, zinc acetate, cadmium acetate, aluminum acetate or butanoate, tin chloride, tin benzoate, and antimony
30 oxide. Stannous octanote is the preferred catalyst because of its high solubility in the monomers, ease of preparation in anhydrous form, and low toxicity. The amount of catalyst required can vary from approxi- mately 0.02 to 2 percent by weight, based on monomers and is preferably about 0.2 percent. The molecular weight and melt vis-
35 cosities of the copolymers are controllable by the amount of catalyst

and/or chain-transfer agents such as glycolic acid. The reaction temperature of the polymerization is between approximately 100 to 200 C. The least color formation occurs below 140 C and the rate of polymerization is best above 135 C. Since racemic D,L-lactide melts at 5 127 C it is best for conversion of monomer to polymer to polymerize at a temperature above 127 C.

Where clarity and transparency is required, as with OPS offsets, the copolymers of this invention are polymerized in an inert atmosphere above their melting points, which are generally in the 125 to 150 C 10 range. The molten lactide copolymer can be extruded from the polymerizer in strands and rods, quenched, pelletized and stored in bags for use in subsequent molding and extrusion operations.

Similarly, clarity of thermoformed packaging films and shaped articles is achieved by molding and extruding above the copolymer's 15 melting points and fast cooling the fabricated item. Thereafter, the copolymers remain transparent unless heated for several hours above their glass transition temperature, Tg, and below the melting point, Tm. Slow cooling of thermoformed sheets, slabs, films, and molded items can induce spherulite crystallinity in the copolymers which gains 20 improvement in the heat stability of the fabricated item, but causes some loss of transparency. Nucleating agents such as sodium benzoate, calcium lactate, and the like, can also induce rapid and substantial crystallinity. A modest amount of drawing of the copolymer, between its Tg and Tm, induces orientation of the polymer molecules and can 25 substantially improve physical properties without loss of transparency.

Blending of different types of lactide polymer or copolymer can substantially change the physical properties. As an example, the melt-blending of the high-melting L-lactide polymer with a lower melting lactide copolymer can provide a transparent material which has a 30 sufficient amount and type of crystallinity to remain transparent. Those skilled in the art will recognize that transparency in molded films, great stiffness, elevated heat distortion temperature, thermo-processibility, and environmental biodegradability are a rare combination of properties. Thus, the polymers can be blended, as well 35 as nucleated, oriented, and controlled by molecular weight to provide a

- 48 -

great deal of latitude in the processibility and final properties in the final compounded thermoplastic.

The copolymers of the present invention will hydrolyze back to lactic acid in the presence of moisture. In the presence of ambient
5   air and humidity the hydrolysis becomes evident in about 12 to 18 months time. The copolymers then become sticky, somewhat opaque, and very brittle. When immersed in water the copolymers show obvious hydrolysis effects in 1 to 4 months time, depending on the composition, molecular weights, the ambient temperature, their surface-to-volume
10 ratio, and the particular, aqueous environment the copolymers are placed in. Microorganisms can further reduce the lactic acid to carbon dioxide and water. As an approximate measure, the copolymers have a shelf life of several months, but disappear within about a year when thoroughly wet.
15 The following examples are merely illustrative of the present invention. In Examples 1B to 7B, a composition series was prepared and evaluated. It was discovered, in contrast to the prior art, that there are distinct differences in the processing behavior and physical properties of the L-lactide/D,L-lactide copolymers.

20 Example 1B

In a dry, 500 ml, round-bottom flask was charged 160 g of L-lactide (Purac, Inc., "triple-star" grade) and 40 g of racemic D,L-lactide (Purac, Inc., "triple star" grade). This mixture was heated for approximately 1 hour at 123-129 C under a stopper with a continuous
25 nitrogen purge through a stopper inlet and outlet. The monomers form a clear melt, which is mixed thoroughly by swirling the melt. Catalyst solution was prepared and dried by azeotropic distillation, that is, 10 ml of stannous octoate (Polysciences, Inc.) was dissolved in 60 ml of toluene; 10 ml of toluene, with trace water, was distilled to a Dean-
30 Stark trap that was vented via a drying tube. A 0.20 ml quantity of the stannous octoate solution was pipetted into the melt and mixed thoroughly. The nitrogen sweep continues and the melt becomes increasingly viscous over the next 3 hours. Heating continues at 123-127 C for 20-24 hours. The mixture was allowed to cool to room

temperature and the flask cooled further with liquid nitrogen behind a shield. The glass shatters and is removed from the polymer by tapping. The copolymer is clear and colorless and is evaluated in a series of tests shown in Table 1B. Films were compression molded at 170 C in a
5 heated hydraulic press for later tensile testing. Slabs, 1/8 inch thick were molded for impact testing by notched Izod, ASTM, D256 and heat deflection temperature, ASTM, D648. Glass transition temperature (Tg) and melting point (Tm, center of the endotherm) were evaluated by differential scanning calorimetry (DSC).

10 Examples 2B-7B

The procedures of Example 1B were repeated except that the ratio of L- and racemic D,L-lactide were changed as shown in Table 1B with the test results. The pure L-lactide polymer, Example 7B, would not always mold well at 170 - 200 C since it frequently crazed badly on
15 cooling in the mold. Frequently, on cooling, it opacified.

TABLE 1B. PROPERTIES OF L-LACTIDE/RACEMIC D,L-LACTIDE COPOLYMERS

Composition, Weight Ratio, L-Lactide/ D,L-Lactide (Racemic)	80/20	85/15	87.5/12.5	90/10	90/10	95/5	100/0
Example No.	1B	2B	3B	4B	5B	6B	7B
Color/Transparency	colorless & transparent →→→→→→→→→→→→→→						white, opaque
Film Thickness, mil	10	5	15	11	5	10	5
Tensile Strength, 1000 psi, ASTM D882	7.9	6.9	8.3	8.6	8.2	9.2	(a)
Elongation, %	3.5	5.8	6.0	7.1	7.2	5.1	(a)
Tangent modulus, 1000 psi	289	221	694	210	268	748	--
Izod impact strength(b), ft-lb/in.	--	0.44	0.34	0.31	--	0.41	(a)
M_w, 1000's	--	928	--	--	--	--	--
M_n, 1000's	--	218	--	--	--	--	--
T_g, C(c)	53	53	48	44	--	46	--
T_m, C(c)	--	--	125	133	--	152	190

(a) Crazes on cooling, too brittle to test.
(b) Notched samples, impacted on notched side on 1/8 in. thick specimens.
(c) Differential scanning calorimetry in nitrogen with 10 C/min. heating rate.

Example 8B

        Similar to Examples 4B and 5B, a 90/10 weight ratio copolymer of
L-lactide/racemic D,L-lactide was prepared.   Into a dry, nitrogen-
swept, 2-liter flask was placed 1045.8 g L-lactide and 116.4 g of
5   racemic D,L-lactide.   A 1.0 ml quantity of anhydrous stannous octoate
(0.2 ml per ml of toluene) solution was added.   The flask was swept
with nitrogen overnight, then heated in a 141 C oil bath until the
monomers are melted and well mixed, and the heating decreased slowly to
125 C and continued for 72 hours.   The polymer slowly whitens on
10 cooling.   After removing the glass, the cloudy, colorless, glassy
copolymer was evaluated.   Gel permeation chromatography obtains a
weight-average molecular weight (M_w) of 522,000, and a number-average
molecular weight (M_n) of 149,000.

        A DSC of the lactide polymer reveals a strong Tm at 145 C, see
15 Figure 10.   The lactide polymer was melted, quenched, and examined
again by DSC to reveal no crystallization or melting points.   However,
a Tg appears at approximately 50-55 C.   The results show the polymer
can be crystalline or amorphous, depending on its heat history.

Examples 9B - 12B

20   The composition series was extended, using the procedures of
Example 1B except other L- and racemic D,L-lactide ratios were used and
heating was 2 hours 125 C, 14 hours 125-147 C, then 2 hours 147-131 C.
The results are shown in Table 2B.

- 52 -

TABLE 2B.   TENSILE AND MODULUS PROPERTIES OF L-LACTIDE
AND D,L-LACTIDE COPOLYMERS

Composition, weight Ratio, L-Lactide/ D,L-Lactide (Racemic)	70/30	60/40	20/80	0/100
Example No.	9B	10B	11B	12B
Color/transparency	Colorless/ clear			
Film thickness, mil	6-9	4-6	4-5	5-7
Tensile strength,[a] 1000 psi, ASTM D638[a]	6.9	6.7	5.8	5.6
Elongation, %	3.2	3.0	2.7	2.8
Tangent modulus, 1000 psi	287	293	275	278

(a)   Films were pulled at a jaw separation of 0.2"/min. and chart speed of 5"/min.

- 53 -

   The results of the above examples reveal that only certain com-
positions have the required properties for an OPS offset. The main
requirements for an OPS-like material are clarity and colorlessness,
tensile strength greater than 7000 psi, tangent modulus (a measure of
5 stiffness) greater than 400,000 psi and well-behaved thermoplasticity.
Table 3B lists some side-by-side comparisons of a crystal polystyrene
(OPS) and a 87.5 weight percent L-lactide and 12.5 weight percent
racemic D,L-lactide random copolymer.

TABLE 3B.   PHYSICAL PROPERTY COMPARISONS

Property	Poly(lactic acid), Example 3B	Crystal Polystyrene
Impact strength, notched Izod, ft-lb/in.	0.4	0.4
Ultimate tensile strength, psi	8300	7400
Elongation, %	6.0	4.0
Elastic modulus, psi	694,000	450,000
Deflection temperature, F under load, 264 psi	(a)	200
Specific gravity	1.25	1.05
Rockwell hardness	(b)	M75
Vicat softening point, F	(c)	225
Melt flow rate, D1238(G)	40-46(d)	1.7 g/10 min.(e) 1.6 g/10 min.(f)

(a)   Depends on heat history.
(b)   Shore D = 97.
(c)   DSC, T_m = 125 C (257 F) at 10 degree/min.
(d)   Flow rate decreases at lower temperature.
(e)   Listed by manufacturer.
(f)   By our experiment.

- 54 -

Example 13B

    The copolymer of Example 2B was molded and remolded several times to determine if color would develop in the films and the molecular weights remained high. This determines if the copolymer can be
5 recycled, an important consideration for manufacturing practices. The results of Table 4B show that the copolymer remained completely transparent and colorless after repeated heating and molding despite the fact that the copolymer was repeatedly exposed to air at elevated temperatures.

10   TABLE 4B. EFFECT OF MOLDING ON LACTIDE COPOLYMER

Example No.	History	Appearance	M_w, 1000's	M_n, 1000's	M_w/M_n
Example 2B[a]	Not molded, directly from polymerization	Completely transparent and colorless	928	218	--
Example 13B[a]	Ex. 2B after molding[b]	"	301	135	2.22
Example 13B[a]	Ex. 2B after molding 6 times[b]	"	137	56.7	2.42

(a)   85/15, L-lactide/racemic D,L-lactide copolymer.
(b)   Compression molding at 167 C (333 F) for 7 minutes to 5-mil film.

Examples 14B-18B

    The copolymers of Examples 2B, 3B and 6B were compression molded into films of approximately 20 to 30-mil thickness and were placed in a heated Instron tester where the films were drawn 5 times their length
30 at 83 C at a rate of 0.5 inch per minute. The films were cooled quickly upon removal from the Instron, and found to be approximately 5-mil in thickness. They were clear and colorless. Tensile properties were evaluated and are listed in Table 5B. When drawn 8 to 10 times

their length, the films show evidence of crystallinity formation by virtue of haze development and some loss of transparency.

The results demonstrate that very thin films can be made with adequate stiffness and transparency for an OPS offset. Thus, despite 5 the higher density of the lactide copolymers compared to polystyrene, less material can be used for stiff OPS offsets.

TABLE 5B. PROPERTIES OF L-LACTIDE/RACEMIC D,L-LACTIDE COPOLYMERS AFTER ORIENTATION(a)

Composition, weight Ratio, L-Lactide/ D, L-Lactide (Racemic)	85/15	85/15	85/15	87.5/12.5	95/5
Example Number	14B	15B	16B	17B	18B
Film thickness, mil	5.5	5.0	6.5	5.0	4.0
Tensile strength, 1000 psi	14.0	14.7	15.0	13.0	16.0
Elongation, %	31.5	15.4	30.0	23.8	37.4
Tangent modulus, 1000 psi	--	564	419	432	513

(a) 5X oriented at 83 C using a draw down speed of 0.5 in./min. on Instron.

25 Example 19B

Films of the copolymers of lactide of Table 1B were immersed in water for several months interval. The copolymers remained clear for approximately 2 months; after 3 months a slight haziness developed. Upon setting on the shelf in humid air and with frequent handling, the 30 films remain virtually unchanged for approximately 1 year although Instron data will show a slow decrease in the strength and elongation after several months. In a landfill, the buried films disappear in 6 months to 2 years, depending on the moisture, pH, temperature,

- 56 -

composition, surface-to-volume ratio, and biological activity of the landfill. All of the films burn with a clean, blue flame.

Example 20B

The lactide copolymer of Example 5B (quenched, compression-molded 5 film) was examined by DSC and found to have less than 2 percent crystallinity, see Figure 5, in the vicinity of 130 C. A 1/8 inch thick sample of the copolymer of Example 5B was annealed in a 185 F oven for 16 hours. The sample turned hazy and the DSC of the sample, see Figure 7 revealed a pronounced increase in the crystallinity. The 10 sample showed a 264 psi heat deflection temperature (HDT) of 90 to 95 C. A similar sample without annealing exhibited a heat deflection temperature of 50 to 55 C, which corresponds to its Tg.

Example 21B

Calcium lactate, 5 weight percent, was blended on a heated mill 15 roll with the lactide copolymer of Example 5B at 170 C for approximately 5 minutes. The blend was stripped off the roll as a sheet and examined. It was stiff, strong, and hazy. Optical microscopy at 82X reveals heterogeneous domains in the size range of from a few microns to 30 microns. DSC reveals a substantial increase 20 in crystallinity in the vicinity of 145 C, see Figure 8, which remain on quenching and reheating. The results, above, comparing Examples 8B, 20B, and 21B, show that nucleating agents are more prompt and efficient in inducing crystallinity in lactide copolymers. Nucleating agents such as salts of carboxylic acids may be used, salts of lactic acid are 25 preferred.

Example 22B

In a 500-ml, 3-neck, round bottom flask, equipped with a mechanical stirrer and a nitrogen inlet and outlet, was placed 180.7 g of L-lactide and 40.2 g of racemic D,L-lactide (both Boehringer and 30 Ingelheim, grade S). The contents of the flask were heated to 110 C under a nitrogen sweep to melt the lactides and 20.1 g of polystyrene (Amoco R3, melt index 3.5 g/10 min.) was added. The polystyrene

swelled highly and partially dissolved with stirring overnight while
advancing the heat to 185 C. The temperature was decreased to 141 C
and 0.2 ml of anhydrous stannous octoate solution (0.2 ml/ml of
toluene) was added. The stirrer was turned off and the lactides
5 allowed to polymerize at 141 C over 3 days time. The highly swollen,
polystyrene floats to the top after turning off the stirrer. The
lower, polylactide phase was cooled and examined by DSC. The sample
has a low Tg, approximately 35 C, and is otherwise lacking in apparent
temperature   transitions.   Compression-molded   films   are   clear,
10 colorless, and very pliable.   These results indicate that the
polystyrene thoroughly interrupts crystallinity formation.

Example 23B
        The lactide copolymer of Example 8B was mill-roll blended with 20
weight percent of the homopolymer of L-lactide produced in Example 7B.
15 A sample of the homopolymer was analyzed by DSC, see Figure 11. The
blended sample was examined by DSC and found to have a Tg of 59-63 C
and strong Tm's at 150 and 166 C, see Figure 12. Films were clear to
slightly hazy, depending on their cooling rate after pressing.
Quenched samples easily crystallize on heating to approximately 80 - 90
20 C. As a result the heat deflection temperature of the blend is now
quite high. The blend becomes hazy at 80-90 C but does not deflect
with heat as does the unblended 90/10 copolymer. Tensile data as shown
in Table 6B were obtained on unoriented, compression-molded films and
compared to similarly obtained data for polystyrene.

- 58 -

TABLE 6B.   COMPARISON OF BLEND OF POLYLACTIDE OF EXAMPLE 23B
            WITH CRYSTAL POLYSTYRENE

	Example 23B[a]	Crystal Polystyrene[a,b]
Film thickness, mil	8	14
Tensile strength, ASTM D882, 1000's psi	7.7	6.0
Elongation, %, to yield	6.5	3.2
Tangent modulus, 1000,'s psi	323	267

(a) Thin films, unoriented, compression-molded specimens
(b) Melt Index 1.7

This example illustrates that melt blending is an excellent way to improve the properties of the copolymer so that advantageous properties similar to polystyrene are realized. The higher the amount of homopolymer based on L-lactide (or D-lactide) blended with the polymer the higher will be the heat deflection temperature, however, haziness will also increase. Thus addition of homopolymer may be combined with other methods of increasing polystyrene like properties while still retaining clarity

As a further example orienting films produced from the polymer increases the tensile properties. At eight to ten times the draw the physical properties are still increasing but the material becomes hazy. The degree of orientation will thus need to be controlled and combined with the other property changing methods to achieve optimum polystyrene like characteristics.

Examples 24B-27B

Examples 24B to 27B were polymerizations of lactide with controlled amounts of chain transfer agents, demonstrating that molecular weights can be controlled using transfer agents such as glycolic acid. The results are shown in Table 7B. A nearly straight

line relationship exists between the amount of transfer agent and the reciprocal of the weight average molecular weight. A preferred chain transfer agent is lactic acid.

TABLE 7B.   MOLECULAR WEIGHT CONTROL USING CHAIN TRANSFER AGENTS

Example No.	PPH of[a] CTA	M_n[b]	M_w[b]	M_w/M_n
24B	0.22	13,500	107,300	8.0
25B	0.45	12,800	66,700	5.2
26B	0.90	7,300	29,900	4.1
27B	1.80	4,700	13,900	2.9

(a) Parts of glycolic acid chain transfer agent (CTA) per hundred parts of lactide in polymerization recipe.

(b) Gel permeation chromatography in tetrahydrofuran solvent, 23 C, with 10^6, 10^5, 10^4, and 10^3 anhstrom columns, number average, M_n, and weight average, M_w, molecular weights are calculated compared to monodisperse polystyrene standards.

Example 28B

A 4.0 mil, compression-molded film of the lactide copolymer of Example 2B was evaluated as a barrier film by ASTM methods. The results are shown in Table 8B. The lactide copolymer is a much better barrier to carbon dioxide and oxygen than is polystyrene. By comparison to some other polymer barrier films, the lactide copolymer is an adequate barrier film for many packaging applications.

- 60 -

TABLE 8B.   EXAMPLE 28B PERMEABILITY TO GASES[a]

Units	Lactide Copolymer, Example 2B	Crystal[b] Polystyrene	Terephthalate	Vinyldiene[b] Chloride-vinyl Chloride Copolymer
cc/100 sq. in./ 24 hr/atmos				
CO_2	32.1	900	15-25	3.8-44
O_2	19.9	350	6-8	0.8-6.9

(a) ASTM D1434-75, Example 2B was a 4.0 mil, compression-molded film.
(b) Values from Modern Plastics Encyclopedia.

Example 29B

Sheets, 1/8 inch thick of the lactide copolymers of Examples 1B-6B were immersed overnight in a mixture of petroleum ether and methylene chloride.   At ratios of 70/30 to 60/40, petroleum ether/methylene chloride, the copolymers would foam when placed in boiling water. Irregular, but well expanded, foams would form.

Example 30B

A comparison was made of the melt viscosities of a commercial, crystal polystyrene (Type 201, Huntsman Chemical Corp.) and the lactide polymer of Example 8B. The melt index, ASTM D1238 (G), of the polystyrene was 1.6 g/10 min. at 200 C using the standard 5 Kg weight. The melt index of the lactide polymer was 40-46 g/10 min. under the same conditions, however, at 160 C the value was 8.0 g/10 min. A more detailed comparison of melt viscosities was obtained by observing the melt viscosities of the two polymers in an Instron Capillary Viscometer.   The comparative results are shown in Figure 9.   The shear rates normally encountered during extrusion and injection molding are approximately 100 to 1000 reciprocal seconds. Inspection of the data

of Figure 9 shows that the melt viscosity of the lactide polymer at 160 C is very similar to that of the polystyrene at 200 C.

The above results illustrate that lactide polymers can be melt-processed, at lower temperatures than polystyrene, by very similar methods.

Examples 31B-34B

Small, test polymerizations of purified (recrystallized and dried) mesolactide (meso D,L-lactide) were carried out as the homopolymer and the copolymer. The molecular weights were evaluated by GPC and compared to analogues of D,L-lactide. The results are presented in Table 9B. The polymers were melt pressed into films and their physical properties evaluated and compared as shown in Table 10B. Within experimental differences of sheet thickness and molecular weight, the copolymers are similar within experimental error. The homopolymer of mesolactide is somewhat weaker.

TABLE 9B.   GPC MOLECULAR WEIGHT COMPARISONS OF MESO-AND
RACEMIC LACTIDE POLYMERS AND COPOLYMERS

Example Nos.	Composition	Res. Mon., %	GPC x 10^{-3}			
			M_n	M_w	M_z	M_w/M_n
31B	D,L-PLA	--	97.5	341	757	3.49
32B	Meso PLA	2.76	62.5	152	264	2.42
33B	90/10, L-/meso	1.67	29	142	301	1.67
34B	90/10, L-/D,L	--	91.3	201	350	2.20

TABLE 10B. PHYSICAL PROPERTY COMPARISON OF D,L- AND MESO-LACTIDE
POLYMERS AND COPOLYMERS(a)

Example No.	Polymer Composition	Elastic Modulus, 100 psi	Tensile at Yield Strength 100 psi	Elongation to Yield %	Film Thickness, mil	Strain Rate in./min.
31B	Homopolymer of D,L-lactide	278	5.6	2.8	5-7	0.25
32B	Homopolymer of meso-lactide	345	3.8	3.5	9	0.25
33B	90/10, L-/meso lactide copolymer	190	7.9	3.8	12-15	0.25
34B	90/10, L-/D,L- lactide copolymer	323	8.6	4.6	4-6	0.25

(a) Compression-Molded films

An overall description of the composition of the second embodiment
of the invention includes an environmentally biodegradable polymer
comprising polymerized lactic acid units of the structure of formula I,
where n is an integer between 75 and 10,000 and the alpha carbon is a
5   mixture of L- and D-configurations with a preponderance of either D- or
L-units, wherein the polymer is suitable for replacement of
polystyrene. The D- and L-units of the polymer may preferably be
prepared from L-lactide or D-lactide, at 85 to 95 parts by weight, and
D,L-lactide at 15 to 5 parts by weight.

10   An environmentally biodegradable composition with improved
properties more like those of polystyrene comprises blends of a
physical mixture of polymerized lactic acid units of the structure of
formula I, where n is an integer between 75 and 10,000 and the alpha
carbon is a random mixture of L- and D-configurations with a
15   preponderance of either D- or L-units, a lactide hompolymer of D-
lactide or L-lactide. Compositions having n equal to an integer
between 150 and 10,000 have a good balance between strength and melt
processability.

A general description of the process for producing the composition
20   of the second embodiment comprises mixing with a catalyst, heating, and
melting L-lactide or D-lactide monomer and D,L-lactide monomer whereby
the L-lactide monomer or D-lactide monomer is in an amount of 85 to 95
parts by weight and D,L-lactide monomer is in an amount of 15 to 5
parts by weight, to form an intimate solution; polymerizing the
25   solution; and treating the polymer to modify its properties so as to
make the polymer suitable as a replacement for polystyrene. The
properties of the composition may be adjusted by adding a nucleating
agent; adding a D-lactide or L-lactide homopolymer by blending to
produce a physical mixture; orienting the polymer; adding a nucleating
30   agent and a D-lactide or L-lactide polymer by blending; adding a
nucleating agent and a D-lactide or L-lactide polymer by blending and
orienting the polymer; adding chain transfer agents to the polymeriza-
tion step so as to adjust the characteristics to a polystyrene
replacement, annealing at an elevated temperature, and adding

- 64 -

additional plasticizer where the plasticizer is selected from the group consisting of D-lactide, L-lactide, meso D,L-lactide, lactic acid, lactide oligomer, lactic acid oligomer, and mixtures thereof. If a monomer is selected as a plasticizer a unique composition may be

5 obtained by adding monomer that is stereochemically different from that used to obtain the polylactide in the composition. Similarly, addition of oligomer stereochemically different from that which may be obtained during polymerization of the polymer gives a unique product. Color bodies can be excluded by performing the polymerization in an inert

10 atmosphere and at reaction temperatures preferably at 140 C or below. Various combinations of the above treatments can be employed to obtain the optimum characteristics as those skilled in the art will appreciate, once knowing the teachings of the invention.

As can be noted in the aforementioned first embodiment, a higher

15 amount of monomer or oligomer can have significant effect. In the present second embodiment lower amounts of monomer and oligomer are preferred to impart stiffness. Plasticizer present in an amount of 0.1 to 5 percent is preferred. The composition usually contains plasticizer in an amount that depends on polymerization conditions or

20 on the amount added after polymerization. The additional monomer used as plasticizer may be selected from the group: D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof. Oligomers of lactide or lactic acid may also be added. Unique compositions may be obtained by addition of monomer or oligomer stereochemically

25 different from those selected for the polymers in the composition.

Further provided by the second embodiment of the invention is a method for replacing a thermoplastic composition with the biodegradable composition of the invention where the thermoplastic composition comprises first orientable polystyrene units, by replacing

30 the first polymer units with a second orientable polymer having an unoriented tensile strength of at least 5,000 and a tangent modulus of at least 200,000; wherein the second polymer comprises polylactic acid units of the structure in formula I, wherein n is the number of repeating units and n is an integer, $75 \leq n \leq 10,000$, and the alpha

35 carbon is a mixture of L- and D- configurations with a preponderance of

either D- or L- units, wherein the polymer is prepared from L- or D-lactide at 85 to 95 parts by weight, and D,L-lactide at 15 to 5 parts by weight and is plasticized with a plasticizer selected from the group consisting of lactide, oligomers of lactic acid, oligomers of lactide
5   and mixtures thereof between 0.1 and 5.0 weight percent.

Contemplated equivalents of the compositions of the invention are those that contain minor amounts of other materials. The compositions produced in accordance with the present invention can be modified, if desired, by the addition of a cross-linking agent, other plasticizers,
10   a coloring agent, a filler and the like.

The compositions herein can be processed by melt fabrication into useful articles of manufacture having a self supporting structure such as disposable containers, eating utensils, trays, plates, drinking cups, single serving trays, syringes, medical trays, packaging films
15   and the like. The compositions are useful in that they can have the characteristics of the usual polystyrenes and therefore substitute for them yet degrade in the environment. The compositions are especially useful for articles having only a one time use or a short life span in use before disposal.

20   Third General Embodiment

A third embodiment discloses the blending of polylactic acid (PLA) with polystyrene (PS), polyethylene (PE), polyethylene terephthalate (PET), and polypropylene (PP). The embodiment discloses that polylactic acid is melt compatible with these conventional
25   thermoplastics and the effect on their physical properties.

The environmentally degradable compositions disclosed herein are at least partially degradable. That is the polylactic acid portion of the composition will decompose relatively rapidly compared to the more stable portions of the blend and cause a physical deterioration of the
30   blended material. For example, when the compositions are intimate and homogeneous blends with small domain sizes the physical deterioration will destroy the original formed product. The compositions herein provide environmentally acceptable materials because their physical deterioration and degradation is much more rapid than conventional

- 66 -

nondegradable plastics.   Further, since a significant portion of the
composition can be polylactic acid, and/or a lactic acid derived
lactide or oligomer only a small portion of more slowly degrading
thermoplastic residue will remain (e.g. polystyrene).   This residue
5   will have a high surface area and is expected to decompose faster than
a bulk formed product.

D-lactide is a dilactone, or cyclic dimer, of D-lactic acid.
Similarly, L-lactide is a cyclic dimer of L-lactic acid.   Meso D,L-
lactide is a cyclic dimer of D- and L-lactic acid.   Racemic D,L-lactide
10   comprises a 50/50 mixture of D-, and L-lactide.   When used alone
herein, the term "D,L-lactide" is intended to include meso D,L-lactide
or racemic D,L-lactide.   Polylactic acid may be prepared from one or
more of the above.

Example 1C

15   Polystyrene was solvent blended with polylactic acid and solvent
cast from CH_2Cl_2 to determine optimum compatibility.   The solvent cast
films were translucent and apparently "noncheesy".   A sample, appears
homogeneous to the naked eye and resists folding and handling without
shredding apart.   Optical microscopy at 310X reveals heterogeneous
20   domains of 3 microns and less.   The blend is apparently very com-
patible.   It exhibits no change over 2 years with regard to "blooming"
of fugitive material nor does its physical properties show evidence of
degradation.

Example 2C

25   Polypropylene 8525, Hercules, was similarly melt blended in the
Brabender with polylactic acid at 400 F.   Ratios of PP/PLA prepared
were 100/0 for the control, 90/10, and 75/25.

Examples 3C-5C

Melt blends were prepared of polylactic acid with polystyrene.
30   Both a high molecular weight polystyrene (Piccolastic, E-125, Hercules)
and a low molecular weight polystyrene (Piccolastic, D-100) were
investigated.   Also used was a general purpose polystyrene, (Huntsman

polystyrene 208), a crystal polystyrene. These were mixed in a Brabender at 325 F at different ratios with polylactic acid.

The polystyrene/polylactic acid ratios used were 100/0 for the control, and 90/10, and 75/25 for the Huntsman 208, general purpose
5 polystyrene.

Examples 6C-7C

Two types of polyethylene terephthalate were used. (Goodyear's "Clearstuff" and Eastman's Kodapak TN-0148). These were dried overnight at 90 C and melt blended at 525 F in a Brabender with
10 polylactic acid for only a few minutes. The polylactic acid reduced the melt viscosity.

Examples 8C-16C

The controls and blends for polypropylene, general purpose polystyrene, and polyethylene terephthalate (Eastman's) from Examples
15 2C-7C were ground in an Abbey grinder and compression molded into approximately 5 mil films. Polypropylene-polylactic acid films were molded at about 400 F; polystyrene-polylactic acid films were obtained at 250-300 F; polyethylene terephthalate-polylactic acid films were molded at about 525 F. After conditioning at 50 percent r.h. and 23 C
20 for 24 hours they were tested on the Instron. The controls were similarly treated. Samples of the compression molded film were placed in an Atlas Weather-O-Meter for weatherability evaluation (cycles of 102 minutes of sunshine and 18 minutes of rain). The results for these Examples are shown in Table 1C.

25 Examples 17C-19C

Three samples of 100 percent polylactic acid using poly (D,L-lactic acid) were prepared as above but with film thicknesses of 10-15 mil. Tests were performed as in Examples 20C-27C below except that the second sample was tested after 82 hours of exposure to 50 percent
30 relative humidity at 72 F.

Examples 20C-27C

   High density polyethylene, HDPE, (0.960 g/cc) was melt blended
with polylactic acid in the Brabender Plasticorder at 151 C for 10
minutes. Blend ratios of high-density polyethylene/polylactic acid of
5   100/0 for the controls, 90/10, 80/20, and 50/50 were used. Two samples
of each were prepared. The blends were ground in an Abbey grinder and
compression molded into 10-15 mil films. The films were tested in an
Atlas Weather-O-Meter set for 51 minutes of carbon arc light and 9
minutes of water spray. Temperature was varied from ambient to 140 F.
10 Tensile strengths, elongation to yield tests and classification of the
tensile failure were performed for the samples as shown in Table 2C.

Examples 28C-33C

   Low density polyethylene, LDPE, (0.917 g/cc) was melt blended with
polylactic acid in the Brabender Plasticorder at 151 C for 10 minutes.
15 Blend ratios of low density polyethylene/polylactic acid of 100/0 for
the controls 90/10 and 50/50 were used. Two samples of each were
prepared. The samples were treated and evaluated as in the case of
Examples 20C-27C. Results are shown in Table 2C.

Example 34C

20   In a 500-ml, 3-neck, round bottom flask, equipped with a mechan-
ical stirrer and a nitrogen inlet and outlet, was placed 180.7 g of L-
lactide and 40.2 g of racemic D,L-lactide (both Boehringer and
Ingelheim, grade S). The contents of the flask were heated to 110 C
under a nitrogen sweep to melt the lactides and 20.1 g of polystyrene
25 (Amoco R3, melt index 3.5 g/10 min.) was added. The polystyrene
swelled highly and partially dissolved while stirring overnight and
advancing the heat to 185 C. The temperature was decreased to 141 C
and 0.2 ml of anhydrous stannous octoate solution (0.2 ml/ml of
toluene) was added. The stirrer was turned off and the lactides
30 allowed to polymerize at 141 C over 3 days time. The highly swollen,
polystyrene floated to the top after turning off the stirrer. The
lower, polylactide phase was cooled and examined by differential
scanning calorimetry (DSC). The sample has a low Tg, approximately 35

C, and is otherwise lacking in apparent temperature transitions. Compression-molded films are clear, colorless, and very pliable. These results indicate that the polystyrene thoroughly interrupts crystallinity formation under these conditions.

5   Example 35C

Polylactic acid was mill roll blended with crystal polystyrene. The blend revealed excellent compatibility of polystyrene dispersed in polylactic acid. Thus 5 weight percent of polystyrene was dispersed in a 90/10 ratio of L-/racemic D,L-lactide copolymer in a two roll mill at 10   170 C. The material became hazy and exhibited considerable crystallinity by thermal analysis. This example demonstrates that under these conditions polystyrene easily induces crystallinity in polylactic acid. A thermal analysis of the material, see Figure 13, reveals that the material remains crystalline even when heated and 15   cooled.

The Examples 34C and 35C illustrate that polylactic acid blended with the environmentally nondegradable plastics herein can produce final properties in the mixture depending on the mixing or blending technique used.

20   Brabender melt-blends of all types exhibited small heterogeneous particle sizes of 10 microns or less. The tensile strengths were evaluated before, and after, simulated weathering. After 1248 hours (52 days) in the Atlas Weather-O-Meter all of the polypropylene samples were whitened, extremely brittle and were not able to be tested. The 25   polypropylene samples were retested at shorter intervals as shown in Table 1C. At approximately 300 hours of weathering in the Atlas Weather-O-Meter, the samples exhibited significant environmental degradation.

The polystyrene blends with polylactic acid exhibited 30   environmental degradation that was apparent after 300 hours of simulated weathering. The polyethylene terephthalate blends were also visibly environmentally degraded in approximately 300 hours.

TABLE 1C.   TENSILE STRENGTH OF FILMS BEFORE, AND AFTER ACCELERATED WEATHERING[a]

Blend Ratio and Material	Tensile Strength[b]/% Elongation		
	Before	After, hrs	
		310	400
100/0 PP/PLA[c]	1665/61	585/1.6	494/1.7
90/10, PP/PLA	1568/51	954/3.2	346/--
75/25, PP/PLA	1124/14	370/1.1	254/1.0
100/0 PP/PLA[d]	3200/2.0	1066/1.0	--
90/10, PS/PLA	2350/2.0	582/1.0	--
75/25, PS/PLA	1493/1.6	484/1.0	--
100/0 PET/PLA[e]	3036/--	3509/3.0	--
90/10, PET/PLA	2147/--	1378/3.0	--
75/25, PET/PLA	2743/--	2041/3.0	--

(a)   Weather-o-meter, cycle of 102 minutes of sunshine, 18 minutes of rain.
(b)   0.05 in./min., on the Instron.
(c)   Hercules polypropylene 825.
(d)   Huntsman 208.
(e)   Tennessee Eastman, Kodapak TN 0148.

The polylactic acid, high density polyethylene, low density polyethylene, and their blends were evaluated for physical strength, before, and after simulated weathering and the results are shown in Table 2C.

TABLE 2C. PHYSICAL PROPERTIES OF POLYETHYLENE (PE), POLYLACTIC ACID (PLA), AND THEIR BLENDS, BEFORE, AND AFTER, WEATHER-O-METER EXPOSURES

Material[a]	Material Blend Ratio[b] Polymer/PLA	Weather-O-Meter[c] Exposure, hours	Tensile Strength, psi	Elongation[d] to Yield, %	Type of Tensile Failure
100% PLA[e]	0/100	0	6,030	2.2	Brittle
100% PLA	0/100	0[f]	5,670	2.1	Brittle
100% PLA	0/100	82	(too brittle to test)	--	Brittle
100% HDPE[g]	100/0	0	3,540	8	Ductile
100% HDPE	100/0	233	1,400	1	Brittle
HDPE/PLA	90/10	0	3,480	7	Ductile
HDPE/PLA	90/10	233	1,720	1	Brittle
HDPE/PLA	80/20	0	3,180	4	Brittle
HDPE/PLA	80/20	125	2,150	2	Brittle
HDPE/PLA	50/50	0	2,720	2	Brittle
HDPE/PLA	50/50	233	(too brittle to test)	--	Brittle

a) Compression-molded films, 10-15 mil thickness.
b) Melt-blended in Brabender Plasticorder for 10 minutes, 151 C.
c) 51 minutes of carbon arc light and 9 minutes of water spray for each 1 hour cycle. Temperature varies from ambient to 140 F.
d) Elongation at maximum in strain curve.
e) Poly(D,L-lactic acid), $\{n\}$ = 1.16 dl/g, 25 C, THF.
f) After 82 hours exposure to 50% R.H., 72 F.
g) High density polyethylene, density 0.960 g/cc, melt index 0.6 g/10 minutes.

(CONTINUED)   TABLE 2C.   PHYSICAL PROPERTIES OF POLYETHYLENE (PE), POLYLACTIC ACID (PLA),
AND THEIR BLENDS, BEFORE, AND AFTER, WEATHER-O-METER EXPOSURES

	Material(a)	Material Blend Ratio(b) Polymer/PLA	Weather-O-Meter(c) Exposure, hours	Tensile Strength, psi	Elongation(d) to Yield, %	Type of Tensile Failure
5	100% LDPE(h)	100/0	0	1,320	80	Ductile
	100% LDPE	100/0	125	1,250	67	Ductile
	LDPE/PLA	90/10	0	1,190	31	Ductile
	LDPE/PLA	90/10	125	855	14	Ductile
10	LDPE/PLA	50/50	0	1,160	4	Ductile
	LDPE/PLA	50/50	125	(too brittle to test)	--	Brittle

a) Compression-molded films, 10-15 mil thickness.
b) Melt-blended in Brabender Plasticorder for 10 minutes, 151 C.
c) 51 minutes of carbon arc light and 9 minutes of water spray
   for each 1 hour cycle. Temperature varies from ambient to 140 F.
d) Elongation at maximum in strain curve.
h) Low density polyethylene, density 0.917 g/cc, melt index 0.25 g/10 minutes.

15

The polylactic acid and its blends were much more environmentally degradable than the pure low density or high density polyethylene. The high density polyethylene samples degraded substantially without weight loss while the high density polyethylene-polylactic acid blends

5   exhibited weight loss, particularly where microscopy revealed polylactic acid was exposed at the surface of the films. The high density polyethylene degraded by exposure to actinic light as shown by microscopy.

With all of the samples, increasing the percentage of polylactic

10   acid decreased the tensile strength before, and after, simulated weathering. The incorporation of polylactic acid introduced a faster degradation in blends of polypropylene, polystyrene, polyethylene terephthalate, and high and low density polyethylene. Presumably, the actinic light as well as hydrolysis of the polyesters degrades the

15   polymer. The small size of the spherical, microheterogeneous, domains of the blend are undoubtedly polylactic acid, which is mostly buried. Therefore, polylactic acid hydrolysis is slow. Faster degradation via hydrolysis can be achieved by controlling the location of the polylactic acid. This, in turn, is related to the rheology of the

20   blend during melt blending. The small size of the dispersed, heterogeneous domains indicates good compatibility of the mixed polymers.

In a simulated landfill, where light is excluded, the controls and the blends show much slower rates of degradation. With hydrolysis, alone, the polylactic acid samples slowly whiten, while the blends are

25   qualitatively unchanged for the time period tested.

Conversely, addition of minor amounts of nondegradable thermoplastics to polylactic acid to form compatible blends, using, for example, polypropylene, polystyrene, polyethylene terephthalate and high and low density polyethylene will retard the degradation rate of

30   the polylactic acid. A preferred compositional range is from 80-99 weight percent polylactic acid.

A general description of the environmentally degradable composition comprises blends of a physical mixture of polylactic acid (polylactide), and a polymer selected from the group consisting of a

35   polymer of ethylene terephthalate, a polymer or copolymer of styrene,

- 74 -

ethylene, propylene, vinyl chloride, vinyl acetate, alkyl methacrylate, alkyl acrylate, and physical mixtures thereof. Other possible compositional blends are listed below in the discussion of process embodiments of the invention.

5   The blends preferably use a physical mixture of polylactic acid of formula I, where n is an integer between 75 and 10,000; and a polymer selected from the group consisting of polystyrene, polyethylene, polyethylene terephthalate, and polypropylene and other compositions further discussed below. A preferred composition is that where the

10   polylactic acid comprises 5 to 50 weight percent of the composition. A preferred composition has a polylactic acid content of 10 to 20 weight percent.

The polymers selected from the group above, deemed the added polymer, can be used alone or in combination. The group is not

15   restricted to those cited above since other polymer types are noted as compatible with polylactic acid. These include the polymers and copolymers comprised from the group of ethylene, propylene, styrene, vinyl chloride, vinyl acetate, alkyl methacrylates, and alkyl acrylates. It should be understood that the term copolymers as used

20   herein includes polymers made from mixtures of the monomers in the listed group. Physical mixtures of the polymers and copolymers of the above group are likewise useful in the invention.

The third embodiment further provides for a process for producing the composition includes providing a polylactic acid; selecting a

25   polymer from the group consisting of a polymer of ethylene terephthalate, a polymer or copolymer of styrene, ethylene, propylene, vinyl chloride, vinyl acetate, alkyl methacrylate, alkyl acrylate, and physical mixtures thereof; and blending the polymers. The blending may be by melt blending on a mill roll or by compounding in an extruder or

30   by other mechanical means. The polylactic acid provided preferably has the formula I.

It further provides for a process for producing the composition of the invention includes providing a lactide selected from the group consisting of D-lactide, L-lactide, meso D,L-lactide, racemic D,L-

35   lactide, and mixtures thereof; selecting a polymer from the group

consisting of the polymers or copolymers of styrene, ethylene, ethylene terephthalate, propylene, vinyl chloride, vinyl acetate, alkyl methacrylate, alkyl acrylate, and physical mixtures thereof. The selected lactide and polymer are mixed and heated to melt the lactide

5   and at least partially dissolve the polymer. Finally, the lactide, is at least partially polymerized to obtain a blend of polylactide, unpolymerized lactide monomer and the selected polymer. The polymerization is preferably controlled by monitoring the amount of lactide remaining and stopping the polymerization at the desired level.

10 If desired, the polymerization can be carried to completion. Additional lactide monomer, lactic acid, lactide oligomer, lactic acid oligomer, and mixtures thereof in pliable producing amounts can be added as plasticizers to obtain desired characteristics as taught in the first general embodiment.

15   It will be obvious to those skilled in the art that the proportions of polylactic acid and the added polymer can vary widely depending on their mutual solubilities. Solubilities, in turn, vary with the thoroughness of mixing and the mixing temperature. While placing both the polylactic acid and the added polymer into a mutual

20 solvent solution will obtain intimacy, the use of solvent is impractical for many commercial processes. Physical mixing, such as melt blending on a mill-roll or extruder is more practical, but must be controlled to achieve intimacy, that is, high shear is required to achieve the desired intimacy. Even with intimate mixing different

25 polymers may not be compatible, that is, they may still separate into relatively large heterogeneous domains of, for example, 10 to 100 micron size, or larger. This results in a "cheesy" mixture, or a blend with poor properties. What is surprising is that polylactic acid is easily blend compatible with a wide variety of other polymers,

30 including both polar and nonpolar polymers.

The temperature of the melt blending of the polylactic acid with other polymers may be varied to adjust the proportions of the polylactic acid with one, or more, added polymers. At lower temperatures, the solubilities may not be adequate, while too high a

35 temperature will cause decomposition of the mixture. A general

- 76 -

temperature range is 100 - 220 C, and the preferred range is 130 - 180 C. Equally significant is the melt viscosities of the different polymer components. With increasing molecular weight, the viscosities increase sharply. By controlling the proportions of the polylactic
5 acid and the added polymer, or polymers, the temperature, the mixing type and time, and the molecular weight, a wide range of mixtures can be obtained. Thus, for example, the polylactic acid can be dispersed into the added polymer, or polymers, or vice versa, and the size and geometry of the dispersed phase varied greatly, ranging from discrete
10 spheres to strands of different diameters or lengths. This results in a wide latitude of physical properties and degradation times in the environment. The weight percent ratio of polylactic acid to the selected polymer can be between 99:1 to 1:99.

    Where the lactide monomer is used to dissolve the added polymer
15 and the lactide is subsequently polymerized, the temperature of mixing and polymerizing must be balanced between the mutual solubilities and the reactivity of the lactide. Higher temperatures generally produce lower molecular weight polylactic acid. A further embodiment of the invention is to mix at one temperature and polymerize at another
20 temperature to achieve variations in the geometry of the dispersed phase, as discussed above.

    The compositions herein can be processed by melt fabrication into useful articles of manufacture having a self supporting structure such as disposable containers, eating utensils, trays, plates, drinking
25 cups, single serving trays, syringes, medical trays, packaging films and the like. The compositions are useful in that they can have the characteristics of the usual plastics and therefore substitute for them yet degrade in the environment. The compositions are especially useful for articles having only a one time use or a short life span in use
30 before disposal.

Fourth General Embodiment

    Within the fourth embodiment of the invention are included those impact modifiers which are elastomeric and melt compatible with polylactic acid. By "melt compatible", it is meant all those polymers

which can be intimately mixed with polylactic acid as discussed in the third general embodiment. The mix would result in a substantially homogeneous blend.

5   The environmentally degradable compositions disclosed herein are at least partially degradable. That is the polylactic acid portion of the composition will decompose relatively rapidly compared to the more stable portions of the blend and cause a physical deterioration of the blended material. For example, when the compositions are intimate and homogeneous blends with small domain sizes the physical deterioration

10   will destroy the original formed product. The compositions herein provide environmentally acceptable materials because their physical deterioration and degradation is much more rapid than conventional nondegradable plastics. Further, since a major portion of the composition will be polylactic acid, and/or a lactic acid derived

15   lactide or oligomer only a small portion of more slowly degrading elastomer residue will remain (e.g. segmented polyester). This residue will have a high surface area and is expected to decompose faster than a bulk formed product.

The examples below show the blending of polylactic acid (PLA) with

20   a Hytrel™, a segmented polyester which is a block copolymer of hard crystalline segments of polybutylene terephthalate and soft long-chain segments of polyether glycol. It is shown that polylactic acid is melt compatible with this elastomer and the effect on its physical properties.

25   D-lactide is a dilactide, or cyclic dimer, of D-lactic acid. Similarly, L-lactide is a cyclic dimer of L-lactic acid. Meso D,L-lactide is a cyclic dimer of D- and L-lactic acid. Racemic D,L-lactide comprises a 50/50 mixture of D-, and L-lactide. When used alone herein, the term "D,L-lactide" is intended to include meso D,L-lactide

30   or racemic D,L-lactide. Polylactic acid may be prepared from one or more of the above.

Example 1D

A polylactide copolymer without Hytrel™ segmented polyester was prepared using the procedure from Example 1B of the second general

embodiment of Serial No. 229,939 and tested for Izod impact strength. Results are shown in the Table 1D. For further comparison, Table 1B of the second general embodiment lists the Izod impact strength of other ratios of L-lactide to D-L lactide.

5   Example 2D

Into a 3-neck, 250 ml, round-bottom flask is weighed 10.96 g of D,L-lactide, 108.86 g of L-lactide, and 5.27 g of Hytrel™ 4056 segmented polyester (Du Pont, a thermoplastic elastomer). Hytrel™ 4056 segmented polyester is a polyester elastomer with a Shore D durometer,
10   low flexural modulus, high melt viscosity, a melt index of 7, a sp. gr. of 1.17, a m.p. 334 F, a vicat softening temperature of 234 F, and an extrusion temperature of 340 F - 400 F. The flask is fitted with a mechanical stirrer and a nitrogen inlet and outlet. The contents are heated by means of an oil bath. The Hytrel™ segmented polyester dis-
15   solves in the molten lactides at 170 C. A catalyst solution is prepared by dissolving 10 ml of stannous octoate in 60 ml of toluene and distilling 10 ml into the toluene. A 100 microliter portion of the catalyst solution is injected into the solution of lactide and Hytrel™ segmented polyester. The mixture is stirred under nitrogen at 155 C
20   for approximately 64 hours.

The viscosity increases sharply and the mixture turns cloudy. The product is tough and opaque. Films of 8-9 mil thickness were compression molded at 155 C and the tensile properties measured, as shown in Table 1D.

25   Slabs, 1/8 inch thick, were compression molded and their Izod impact strength measured using a 2 pound pendulum. The results are recorded in the Table 1D where the data are compared to a similar polylactide copolymer of Example 1D without Hytrel™ segmented polyester, and to data for so-called medium-impact polystyrene, Example
30   7D.

Example 3D

800.0 g of L-lactide and 202.3 g of racemic D,L-lactide are copolymerized using 1.0 ml of the catalyst solution by methods similar

to Example 2D, omitting the Hytrel™ segmented polyester. The lactide copolymer is clear and colorless. In a separate polymerization 104.0 g of L-lactide is melt polymerized using 100 microliters of catalyst. The polymer (L-PLA) is white, crystalline, and crazes easily when

5   struck.

An electrically-heated, 2-roll mill is heated to 375 F, then 8.4 g of Hytrel™ segmented polyester and 19.2 g of L-PLA are banded on the roll. To this was added 172.4 of the lactide copolymer. The mixture blends easily and is removed from the rolls, molded, and tested as in

10   Example 2D. The data are recorded in Table 1D.

Example 4D

The lactide copolymer of Example 3D, 80 g, the L-PLA of Example 3D, 10 g, and 10 g of Hytrel™ 4056 segmented polyester are 2-roll, mill-blended as described previously in Example 3D. The blend was

15   tested as before and the data are recorded in Table 1D.

Example 5D

100 g of the blend of Example 3D was further blended with 20 g of Hytrel™ 4056 segmented polyester. The mixture easily mixed on the roll and was apparently quite compatible. The physical properties were

20   measured as described previously and recorded in Table 1D.

Examples 6D and 7D

Typical crystal polystyrene and medium-impact polystyrene were tested and used for comparative controls.

- - - - - - - -

25   The above results clearly indicate that polylactides can be impact-modified. The blends provided significantly higher Izod impact strengths than the crystal polystyrene control and gave slightly lower or equivalent impact strengths compared to medium-impact polystyrene. Those skilled in the art will recognize that the data on impact-

30   strength in Table 1D can be improved further by optimizing the amount and type of impact modifier.

Since polylactides have been shown previously in the third general
embodiment above, to be blend-compatible with numerous other compounds
and thermoplastics, the process of impact-modifying polylactides is
generic to mixtures of polylactides and elastomers that are blend-
5   compatible.   Also, those skilled in the art will recognize that the
data of the Table 1D will improve as the blends are injection-molded,
as opposed to compression-molded, since the former often induces
orientation of the specimens and, consequently, a profound improvement
in impact strength.

TABLE 1D.
PHYSICAL PROPERTY COMPARISONS OF IMPACT-MODIFIED POLYLACTIDES

| Example No. | Composition, weight percent | | | Tensile Strength, psi(b,c) | Elongation, percent | Tangent Modulus, psi | Izod Impact Strength ft-lb/in.(c) |
	Lactide Copolymer	L-lactide Homopolymer	Hytrel™(a)				
1D	80(d)	20	0	7,667	3.4	322,679	0.3-0.4
2D	95.8(e)	0	4.2(f)	8,636	3.1	359,409	0.40
3D	86.2(g)	9.6	4.2(h)	7,823	3.1	346,502	0.51
4D	80.0(g)	10.0	10.0(h)	---	---	---	0.53
5D	71.2(g)	7.9	20.9(h)	---	---	---	0.61
6D(i)	0	0	0	6,118	3.2	267,245	0.18
7D(j)	0	0	0	6,090	4	---	0.7

(a) DuPont Hytrel™ 4056, a thermoplastic polyester elastomer.
(b) ASTM D 882.7-15 mil film thickness.
(c) Compression-molded specimens.
(d) control, 90/10, L-D/L-lactide copolymer.
(e) 91/9, L-D/L-lactide copolymer.
(f) Hytrel™ dissolved in lactide monomers before 170 C polymerization.
(g) 80/20, L-D/L-lactide copolymer.
(h) 2-Roll mill-blend at 185-190 C.
(i) Control, crystal polystyrene, melt-index 1.7.
(j) Control, medium-impact polystyrene

- 82 -

The compositions are useful thermoplastics that can be melt fabricated by conventional processes such as extrusion and molding.

The blends preferably use a physical mixture of polylactic acid of formula I, where n is an integer between 75 and 10,000; and a polymer
5   comprising a segmented polyester. A useful composition is that where the polylactic acid comprises 50 to 99 weight percent of the composition. A preferred composition has a polylactic acid content of 70 to 80 weight percent.

Two embodiments of the general process for producing the
10   composition include (1) melt blending of PLA with a blend compatible polymer that provides improved impact resistance such as a segmented polyester and (2) solution blending during PLA polymerization as in Example 2D where Hytrel™ segmented polyester is dissolved in the PLA. The polylactic acid provided preferably has the formula I. If desired
15   plasticizer in pliable forming amounts may be added to the blend that is selected from the group consisting of lactide monomer, lactic acid oligomer, lactic acid, and mixtures thereof. Addition of the plasticizer will provide additional unique physical properties as discussed in the first, second, and third general embodiments discussed
20   above.

Microscopic examination of the Hytrel™ segmented polyester/polylactic acid mixture revealed that the dispersed Hytrel™ segmented polyester is present in small spherical domains a few microns or less in size. These domain sizes can be adjusted by the mixing
25   conditions such as time, speed of mixing, and temperature.

Therefore, for example, the polymer, or polymers, added to the polylactic acid, should be generally of small, heterogeneous domain size, less than 10 microns, and can be submicroscopic, or dissolved, in the polylactic acid. In addition, this impact modifier must be
30   elastomeric.

While not wishing to be held to any particular theory, it is believed that the present invention provides a continuous matrix of polylactic acid containing intimately mixed microscopic domains of Hytrel™ segmented polyester that act as crack arrestors since the
35   latter is a thermoplastic elastomer compatible with polylactic acid.

For this purpose, the impact modifier must be elastomeric and intimately bound into the polylactic acid as a discrete heterogeneous phase. The added polymer, the impact modifier, can be a thermoplastic elastomer, or a crosslinked rubber, to achieve this elastic behavior.

5 Examples are natural rubber and styrene-butadiene copolymers.

In a test of material placed in water for five months, the material embrittled compared to a material not exposed to water. In addition the water turned acidic indicating breakdown of polylactic acid to lactic acid.' It was further apparent that polylactic acid

10 alone degraded faster than the Hytrel™ segmented polyester/polylactic acid mixture. Thus Hytrel™ segmented polyester can also be used to retard the degradation rate of polylactic acid.

A third component can be added which is compatible with the other components discussed above to achieve improved compatibility. Thus,

15 where the polylactic acid and the impact modifier have poor compatibility, a third component can be added to improve the compatibility. This third component is usually added where it is compatible with the other two, individually, and where the other two, polylactic acid and impact modifier are not very compatible. This

20 works by increasing the interfacial bonding between polylactic acid and elastomeric impact modifier. However, what is surprising is the wide latitude of compatibility of polylactic acid with other polymer types, both polar and nonpolar. This can be referred to in the third general embodiment.

25 The compositions herein can be processed by melt fabrication into useful articles of manufacture such as containers, eating utensils, trays, plates, drinking cups, single serving trays, syringes, medical trays, and the like. The compositions are especially useful for articles having only a one time use or a short life span in use before

30 disposal.

While the invention has been described above with reference to various specific examples and embodiments, it will be understood that the invention is not limited to such illustrated examples and embodiments and may be variously practiced within the scope of the claims

35 hereinafter made.

CLAIMS

We claim:

    1.   An environmentally biodegradable composition useful as a replacement for thermoplastic polymer compositions comprising a polymer
5 of the formula:

$$\left(\!\!-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle O}{\|}}{C} - O\!-\!\right)_n$$
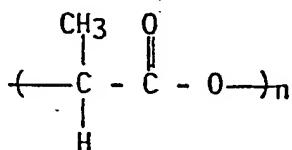
that is plasticized with a plasticizer selected from the group
10 consisting of lactide, oligomers of lactic acid, oligomers of lactide, and mixtures thereof, wherein n is the number of repeating units and n is an integer, $150 \leq n \leq 20{,}000$, and the unoriented composition has a tensile strength of 300 to 20,000 psi, an elongation to failure of 50 to 1,000 percent, and a tangent modulus of 20,000 to 250,000 psi.

15   2.   The composition of Claim 1, wherein the polymer is derived from monomers of lactide selected from the group consisting of L-lactide, D-lactide, meso D,L-lactide, and mixtures thereof.

    3.   The composition of Claim 1, wherein the oligomers of lactic acid or lactide have the formula:

20

$$\left(\!\!-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle O}{\|}}{C} - O\!-\!\right)_m$$

where m is an integer: $2 \leq m < 75$.

    4.   The composition of Claim 1 further comprising additional
25 plasticizer dispersed within the composition that is selected from the group of monomers consisting of D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide and mixtures thereof such that at least part of the dispersed monomer is stereochemically different from that used to prepare the polymer.

5. The composition of Claim 1 further comprising an oligomer dispersed within the composition which is not produced during polymerization of the polymer.

6. A process for producing an environmentally biodegradable
5 composition of polylactic acid comprising:

a. preparing lactide monomer and catalyst;

b. polymerizing the monomer of step (a) to form a polymer at a temperature sufficiently low to allow the reaction to be stopped prior to complete polymerization;

10 c. monitoring the level of monomer in step (b); to determine the amount of monomer remaining; and

d. stopping the polymerization of step (b) prior to complete reaction at an amount of monomer determined in step (c) so that unreacted monomer in a predetermined amount is trapped in
15 association with the polymer.

7. The process of Claim 6 further comprising:

e. incorporating additional plasticizer into the composition whereby the plasticizer is further selected from the group consisting of L-lactide, D-lactide, meso D,L-lactide, lactic acid,
20 oligomers of lactide, oligomers of lactic acid, and mixtures thereof.

8. The process of Claim 7 further comprising selecting a monomer stereochemically different from that selected to prepare the polymer.

9. A process for producing a biodegradable composition of
25 polylactic acid comprising:

a. preparing lactide monomer and catalyst;

b. polymerizing the monomer of the solution of step (a) to form a polymer; and

c. incorporating plasticizer into the polymer of step (b),
30 whereby the plasticizer is selected from the group consisting of D-lactide, L-lactide, D,L-lactide, oligomers of lactic acid, oligomers of lactide, and mixtures thereof.

10. In a thermoplastic polymer composition comprising first orientable polymer units, a method for rendering the composition
35 environmentally biodegradable which comprises:

- 86 -

replacing the first polymer units with a second orientable polymer having an unoriented tensile strength of 300 to 20,000 psi, an elongation to failure of 50 to 1,000 percent, and a tangent modulus of 20,000 to 250,000 psi; wherein the second polymer

5 comprises polylactic acid units of the formula:

$$\left(\!\!-\!\!\begin{array}{c} CH_3 \\ | \\ C \\ | \\ H \end{array}\!\!-\!\!\begin{array}{c} O \\ \| \\ C \end{array}\!\!-\! O\!\!-\!\!\right)_n$$
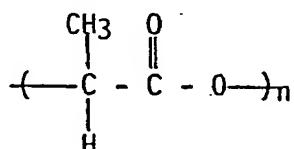
10 wherein n is the number of repeating units and n is an integer, $150 \leq n \leq 20,000$ and is plasticized with a plasticizer selected from the group consisting of lactide, oligomers of lactic acid, oligomers of lactide and mixtures thereof.

11. In a polyolefin composition comprising first orientable
15 polymer units, a method for rendering the composition environmentally biodegradable which comprises:

replacing the first polymer units with a second orientable polymer having an unoriented tensile strength of 300 to 20,000 psi, an elongation to failure of 50 to 1,000 percent, and a tangent

20 modulus of 20,000 to 250,000 psi; wherein the second polymer comprises polylactic acid units of the formula:

$$\left(\!\!-\!\!\begin{array}{c} CH_3 \\ | \\ C \\ | \\ H \end{array}\!\!-\!\!\begin{array}{c} O \\ \| \\ C \end{array}\!\!-\! O\!\!-\!\!\right)_n$$

25 wherein n is the number of repeating units and n is an integer, $150 \leq n \leq 20,000$ and is plasticized with a plasticizer selected from the group consisting of lactide, oligomers of lactic acid, oligomers of lactide and mixtures thereof.

12. An environmentally biodegradable composition useful as a
30 replacement for polystyrene comprising polylactic acid units of the formula:

$$\left(\!\!-\!\!\begin{array}{c} CH_3 \\ | \\ C \\ | \\ H \end{array}\!\!-\!\!\begin{array}{c} O \\ \| \\ C \end{array}\!\!-\! O\!\!-\!\!\right)_n$$

where n is an integer between 75 and 10,000 and the alpha carbon is a mixture of L- and D-configurations with a preponderance of either D- or L-units, wherein the polymer is prepared from L-lactide or D-lactide, at 85 to 95 parts by weight, and D,L-lactide at 15 to 5 parts by weight, where the unoriented polymer has a tensile strength of at least 5000 psi and tangent modulus of at least 200,000 psi and dispersed plasticizer of 0.1 - 5 weight percent.

13.   The composition of Claim 12 further comprising monomer dispersed within the composition that is selected from the group consisting of D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof such that at least part of the dispersed monomer is stereochemically different from the monomer used to prepare the polymer.

14.   The composition of Claim 12 further comprising oligomer stereochemically different from that obtained during polymerization of the polymer.

15.   An environmentally biodegradable composition useful as a replacement for polystyrene comprising blends of a physical mixture of:

a.   a first polymer having polylactic acid units of the formula:
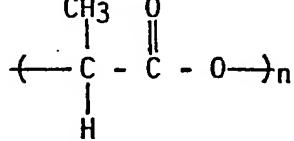
$$\left(\!\!-\!\!\underset{\underset{H}{\overset{}{|}}}{\overset{\overset{CH_3}{|}}{C}} - \overset{\overset{O}{\parallel}}{C} - O\!\!-\!\!\right)_n$$

where n is an integer between 75 and 10,000 and the alpha carbon is a mixture of L- and D-configurations with a preponderance of either D- or L-units; and

b.   a lactide homopolymer of D-lactide or L-lactide; and wherein the unoriented composition has a tensile strength of at least 5000 psi and tangent modulus of at least 200,000 psi and dispersed plasticizer.

16.   The composition of Claim 15 further comprising dispersed plasticizer of 0.1 to 5 weight percent.

17. The composition of Claim 15 wherein the polymerized lactic acid is present in an amount of 98 to 75 weight percent and the lactide homopolymer is present in an amount of 2 to 25 percent.

18. The composition of Claim 15 further comprising plasticizer
5 that is selected from the group consisting of D-lactide, L-lactide, meso D,L-lactide, lactic acid, lactide oligomer, lactic acid oligomer, and mixtures thereof.

19. The composition of Claim 15 further comprising plasticizer that is selected from the group of monomers consisting of D-lactide, L-
10 lactide, meso D,L-lactide, racemic D,L-lactide and mixtures thereof such that at least part of the dispersed monomer is stereochemically different from that used to prepare the first polymer and homopolymer.

20. A process for producing the composition of Claim 12 comprising:
15
    a. mixing with a catalyst, heating, and melting L-lactide or D-lactide monomer, and D,L-lactide monomer whereby the L-lactide monomer or D-lactide monomer is at 85 to 95 parts by weight and D,L-lactide monomer is at 15 to 5 parts by weight, to form an intimate solution;
20
    b. polymerizing the solution of step (a); and
    c. treating the polymer of step (b) to improve its properties.

21. The process of Claim 20 whereby the treatment comprises adding a D-lactide or L-lactide copolymer by blending.
25
22. The process of Claim 20 whereby the treatment comprises adding a nucleating agent, and a D-lactide or L-lactide polymer by blending.

23. The process of Claim 20 whereby the treatment further comprises:
30
    a. controlling the polymerization of step (b) by adding chain transfer agents; and
    b. adding nucleating agents and a D-lactide or L-lactide homopolymer by blending.

24. The process of Claim 20 further comprising the step of
35 treating by adding additional plasticizer to the composition whereby

the plasticizer is selected from the group consisting of D-lactide, L-lactide, meso D,L-lactide, lactic acid, lactide oligomer, lactic acid oligomer, and mixtures thereof.

25.   The process of Claim 20 whereby, when a monomer is selected,

5   at least one monomer is different stereochemically from the monomer(s) selected in step (a).

26.   In a thermoplastic polymer composition comprising first orientable polystyrene units, a method for rendering the composition environmentally biodegradable which comprises:

10   replacing the polystyrene units with a second orientable polymer having an unoriented tensile strength of at least 5,000 psi, and a tangent modulus of at least 200,000 psi and dispersed plasticizer of 0.1 to 5 weight percent; wherein the second polymer comprises polylactic acid units of the formula:

15
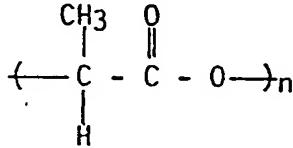
$$\left(\!\!-\overset{\overset{\displaystyle CH_3}{\displaystyle |}}{\underset{\displaystyle |}{\underset{\displaystyle H}{C}}} - \overset{\overset{\displaystyle O}{\displaystyle \|}}{C} - O\!\!-\!\right)_n$$

where n is an integer between 75 and 10,000 and the alpha carbon is a mixture of L- and D- configurations with a preponderance of either D-

20   or L- units, wherein the polymer is prepared from L-lactide or D-lactide, at 85 to 95 parts by weight, and D,L-lactide at 15 to 5 parts by weight.

27.   An environmentally degradable composition comprising blends of a physical mixture of:

25   a.   a polylactic acid; and

          b.   a polymer selected from the group consisting of a polymer of ethylene terephthalate, a polymer or copolymer of styrene, ethylene, propylene, vinyl chloride, vinyl acetate, alkyl methacrylate, alkyl acrylate, and physical mixtures thereof.

30   28.   The composition of Claim 27 wherein the weight percent ratio of polylactic acid to the selected polymer is a ratio between 99:1 and 1:99.

29.   A process for producing the composition of Claim 27 comprising:

a.   providing a polylactic acid;

b.   selecting a polymer from the group consisting of a polymer of ethylene terephthalate, a polymer or copolymer of styrene, ethylene, propylene, vinyl chloride, vinyl acetate, alkyl methacrylate, alkyl acrylate, and physical mixtures thereof; and

c.   blending the polymers of steps a and b.

30.   The composition of Claim 27 further comprising plasticizer that is selected from the group consisting of D-lactide, L-lactide, meso D,L-lactide, lactic acid, lactide oligomer, lactic acid oligomer, and mixtures thereof.

31.   A process for producing an environmentally degradable composition comprising:

a.   providing a lactide monomer selected from the group consisting of D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide and mixtures thereof;

b.   selecting a polymer from the group consisting of a polymer of ethylene terephthalate, a polymer or copolymer of styrene, ethylene, propylene, vinyl chloride, vinyl acetate, alkyl methacrylate, alkyl acrylate, and physical mixtures thereof;

c.   mixing and heating the lactide selected in (a) and the polymer selected in (b) at conditions adapted to melt the lactide and at least partially dissolve the polymer; and

d.   polymerizing the lactide in the mixture of step (c) to obtain a blend of polylactide and polymer.

32.   The process of Claim 31 further comprising the step:

e.   forming the blend into a self supporting structure.

33.   The process of Claim 31 further comprising monitoring the amount of monomer remaining and controlling the polymerization of step (d) to obtain a blend containing residual monomer.

34.   The process of Claim 31 further comprising:

e.   adding plasticizer selected from the group consisting of lactide monomer, lactide oligomer, lactic acid oligomer, lactic acid, and mixtures thereof, to the blend after polymerization.

35.   An environmentally degradable composition comprising blends of a physical mixture of:

a. a polylactic acid; and

b. a blend compatible polymer that provides improved impact resistance to the polylactic acid.

36. The composition of Claim 35 wherein the polylactic acid

5 comprises 50 to 99 weight percent of the composition.

37. The composition of Claim 35 wherein the blend compatible polymer is a segmented polyester.

38. The composition of Claim 37 wherein the blend compatible polymer is a block, copolymer of hard crystalline segments of

10 polybutylene terephthalate and soft long chain segments of polyether glycol.

39. A process for producing the composition of Claim 35 comprising:

a. providing a polylactic acid;

15 b. selecting a blend compatible polymer that increases the impact resistance; and

c. blending the polymers of steps (a) and (b).

40. The process of Claim 39 whereby a segmented polyester is selected.

20 41. The process of Claim 39 whereby a block copolymer of hard crystalline segments of polybutylene terephthalate and soft long chain segments of polyether glycols, or natural rubber and styrene-butadiene copolymers are selected.

42. A process for producing the composition of Claim 35

25 comprising:

a. mixing one or more lactides selected from the group consisting of D-lactide, L-lactide, D,L-lactide and mixtures thereof with a blend compatible polymer that provides improved impact resistance to the composition;

30 b. heating and dissolving the blend compatible polymer in the lactide(s) of step (a) to form a solution; and

c. polymerizing the lactide(s) in the solution.

43. The process of Claim 42 further comprising the step of fabricating the composition into useful forms by melt fabrication.

- 92 -

44. The process of Claim 42 further comprising: Selecting a blend compatible polymer that comprises a segmented polyester.

45. The process of Claim 42 further comprises selecting a blend compatible polymer from the group consisting of a block copolymer of hard crystalline segments of polybutylene terephthalate and soft long chain segments of polyether glycols, and natural rubber and styrene-butadiene copolymers or a mixture thereof.

46. The process of Claim 35 further comprising:

e. adding plasticizer to the blend selected from the group consisting of lactide monomer, lactide oligomer, lactic acid oligomer, lactic acid, and mixtures thereof.

1

FIG. I

FIG. 2

FIG. 3

FIG. 4

3
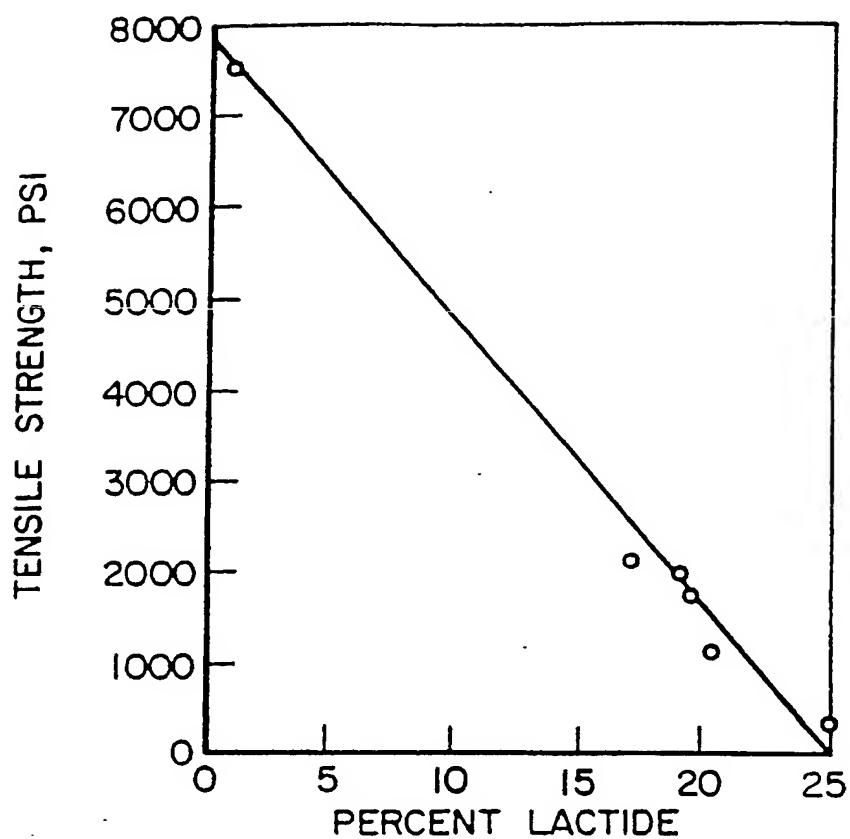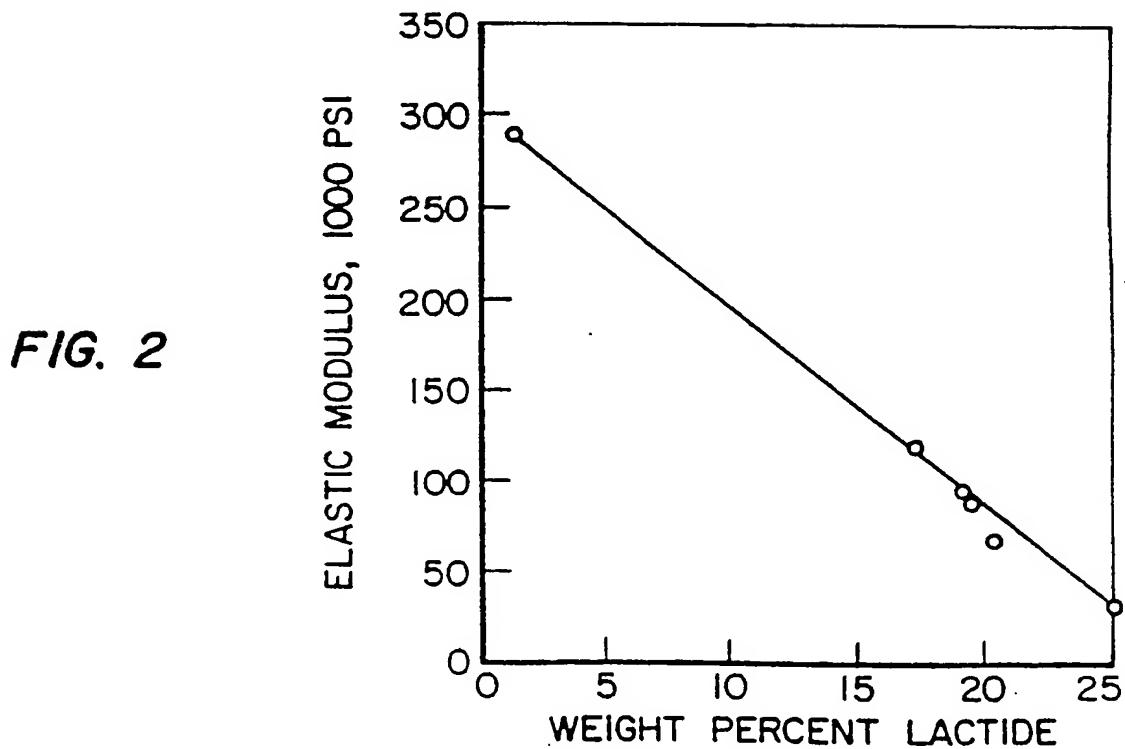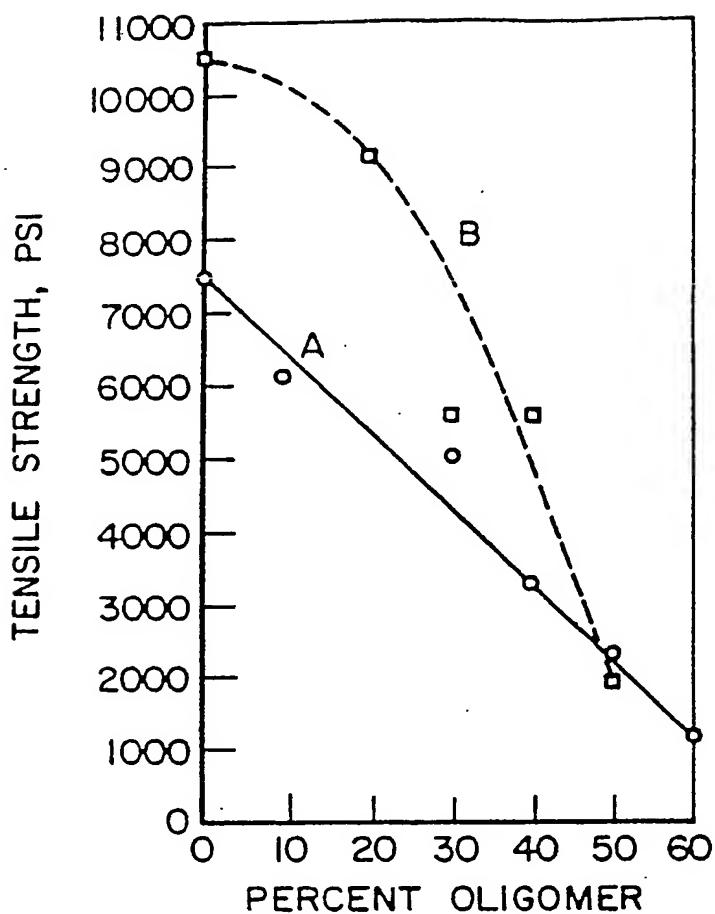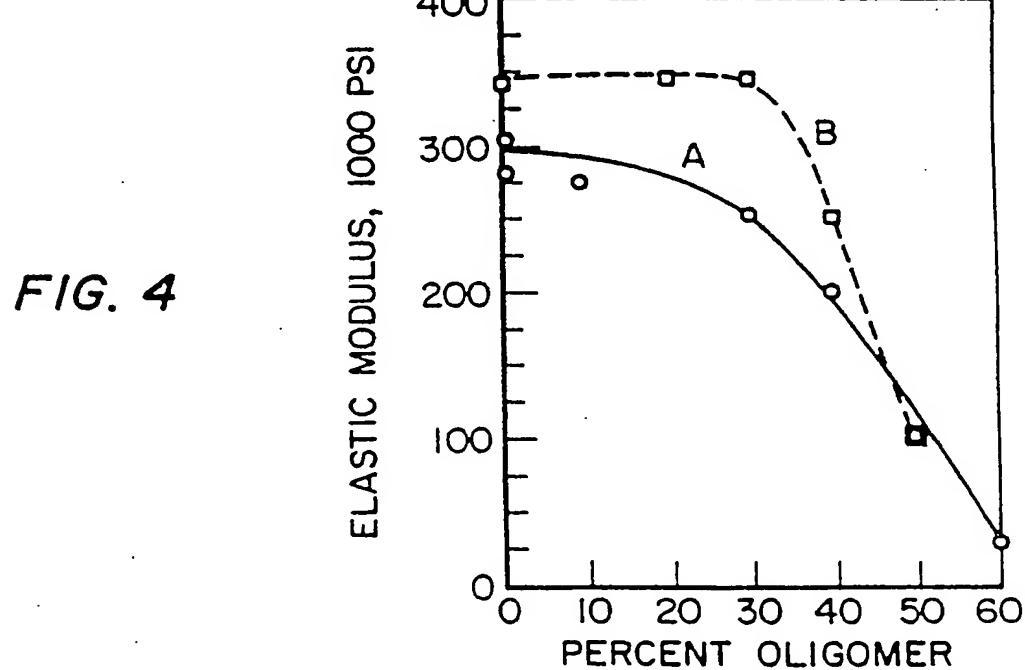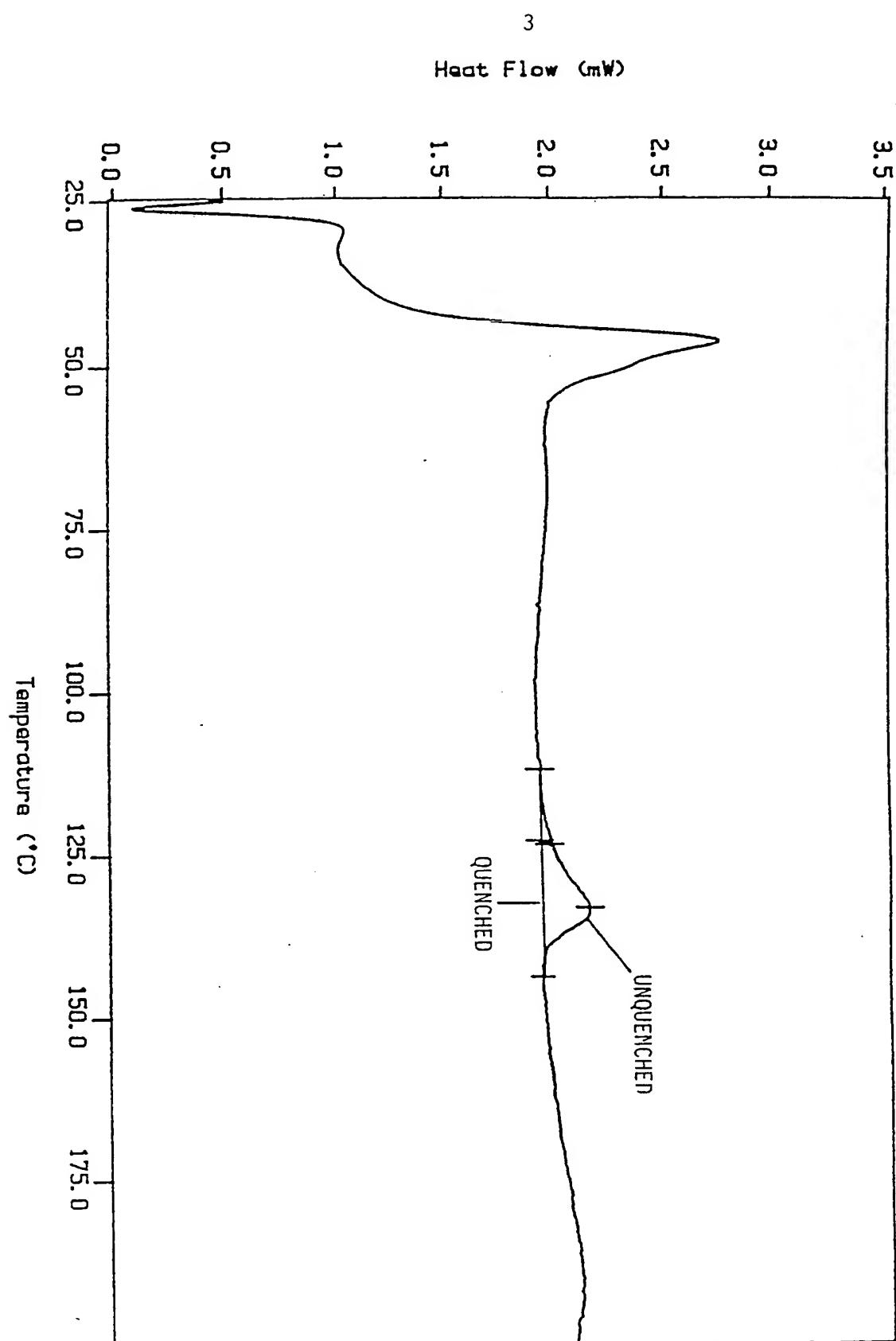
Figure 5.   DSC OF UNANNEALED 90/10; L-/D,L-LACTIDE COPOLYMER

Heat Flow (mW)
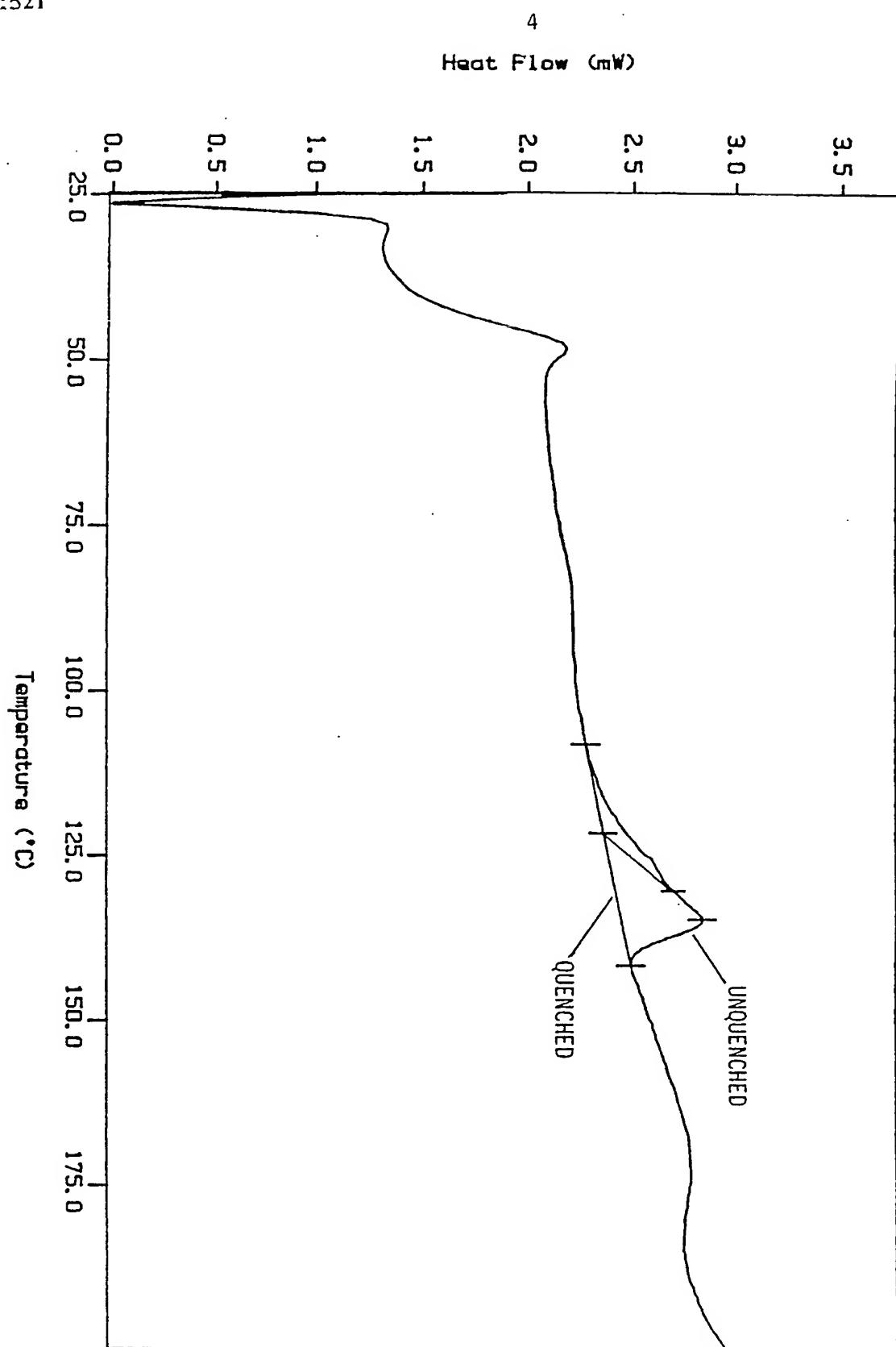
Figure 6: DSC OF SAMPLE OF FIGURE 1 AFTER 100 MINUTES AT 70 C

5
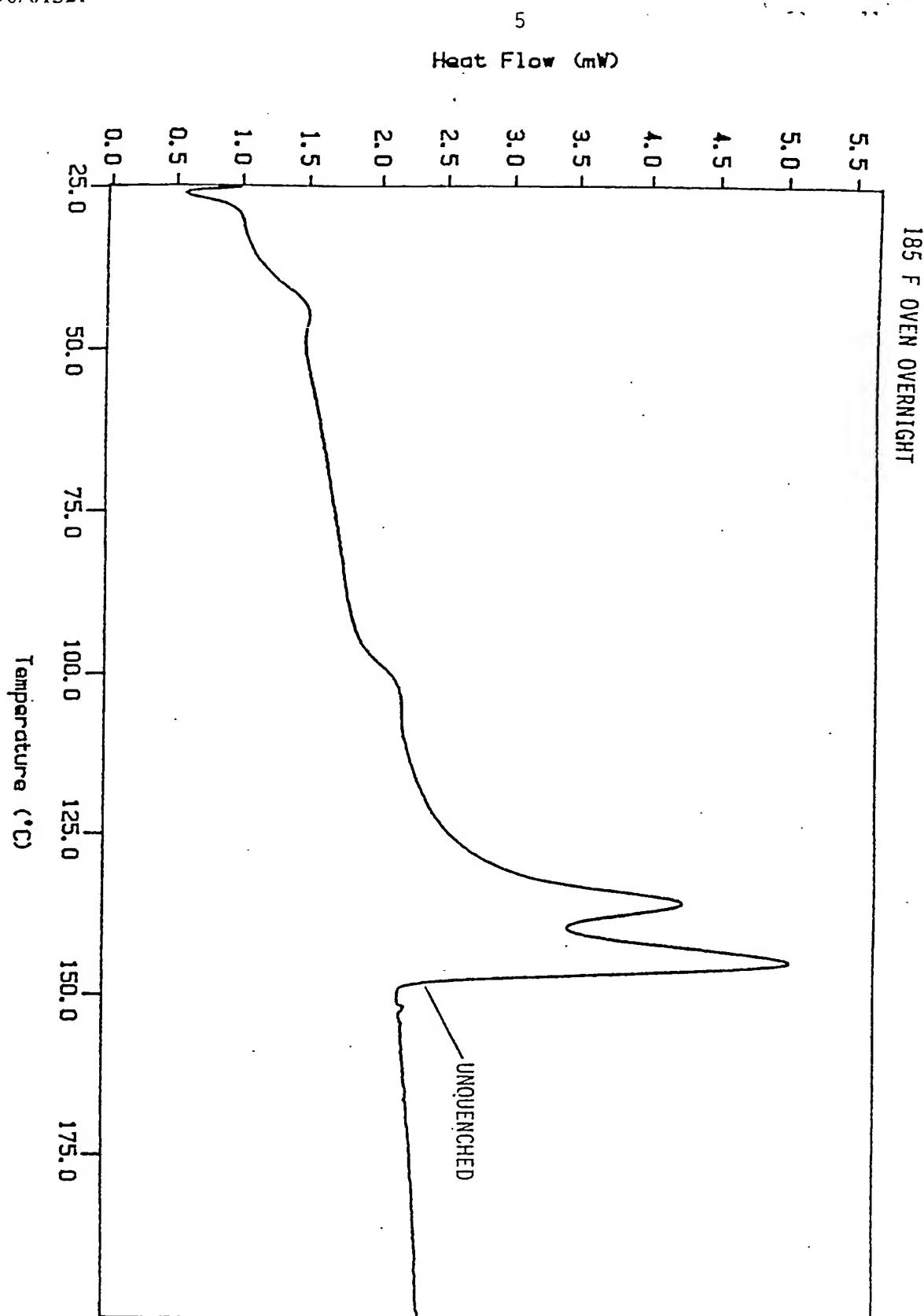
Figure 7.   DSC OF ANNEALED COPOLYMER OF FIGURE 1
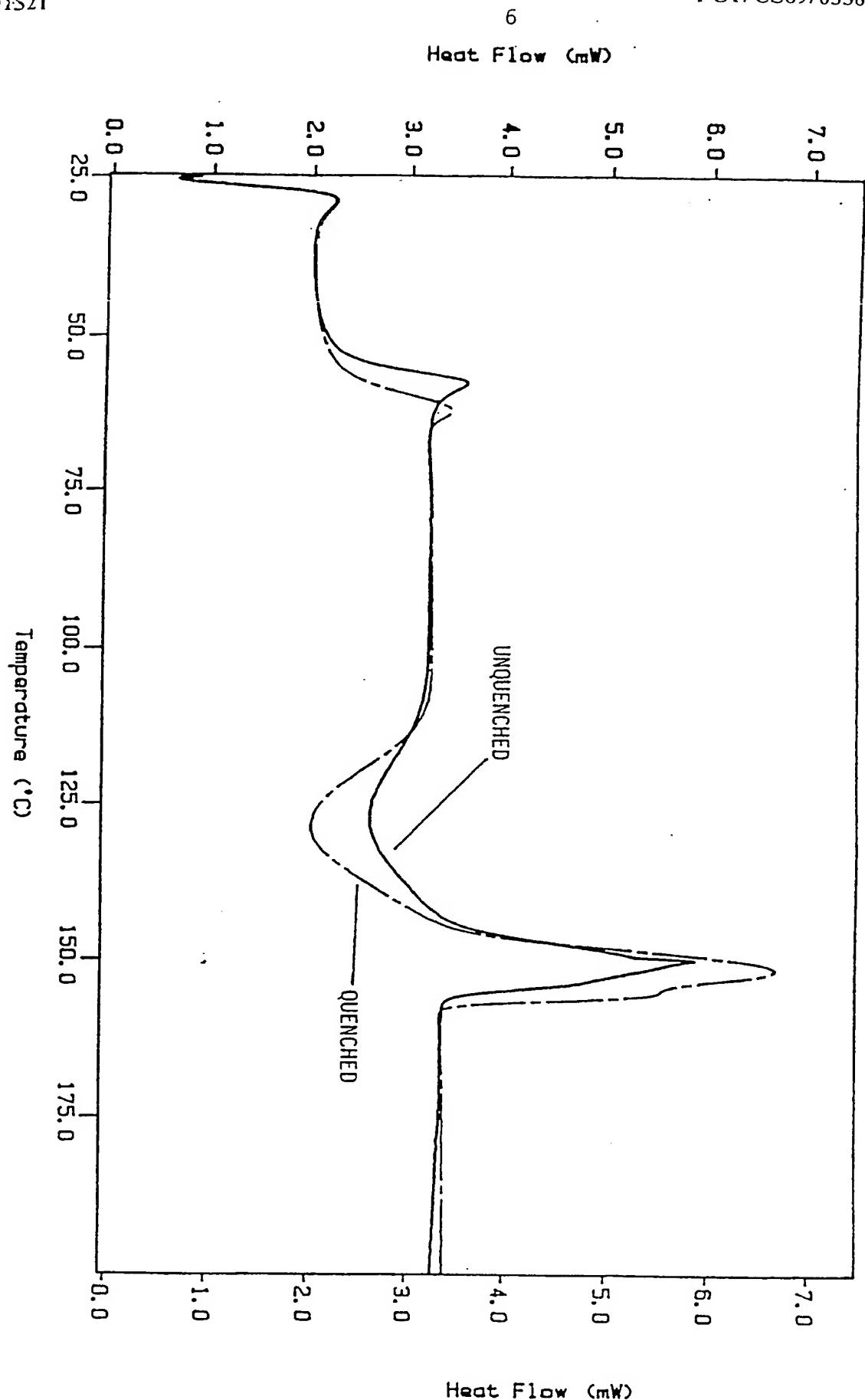
Figure 8. DSC OF 90/10, L-/D,L-LACTIDE COPOLYMER BLENDED
WITH 5 PERCENT CALCIUM LACTATE

7

Melt Viscosity (poise)
(Thousands)

VISCOSITY vs SHEAR RATE

Lactide Polymer of Example #8
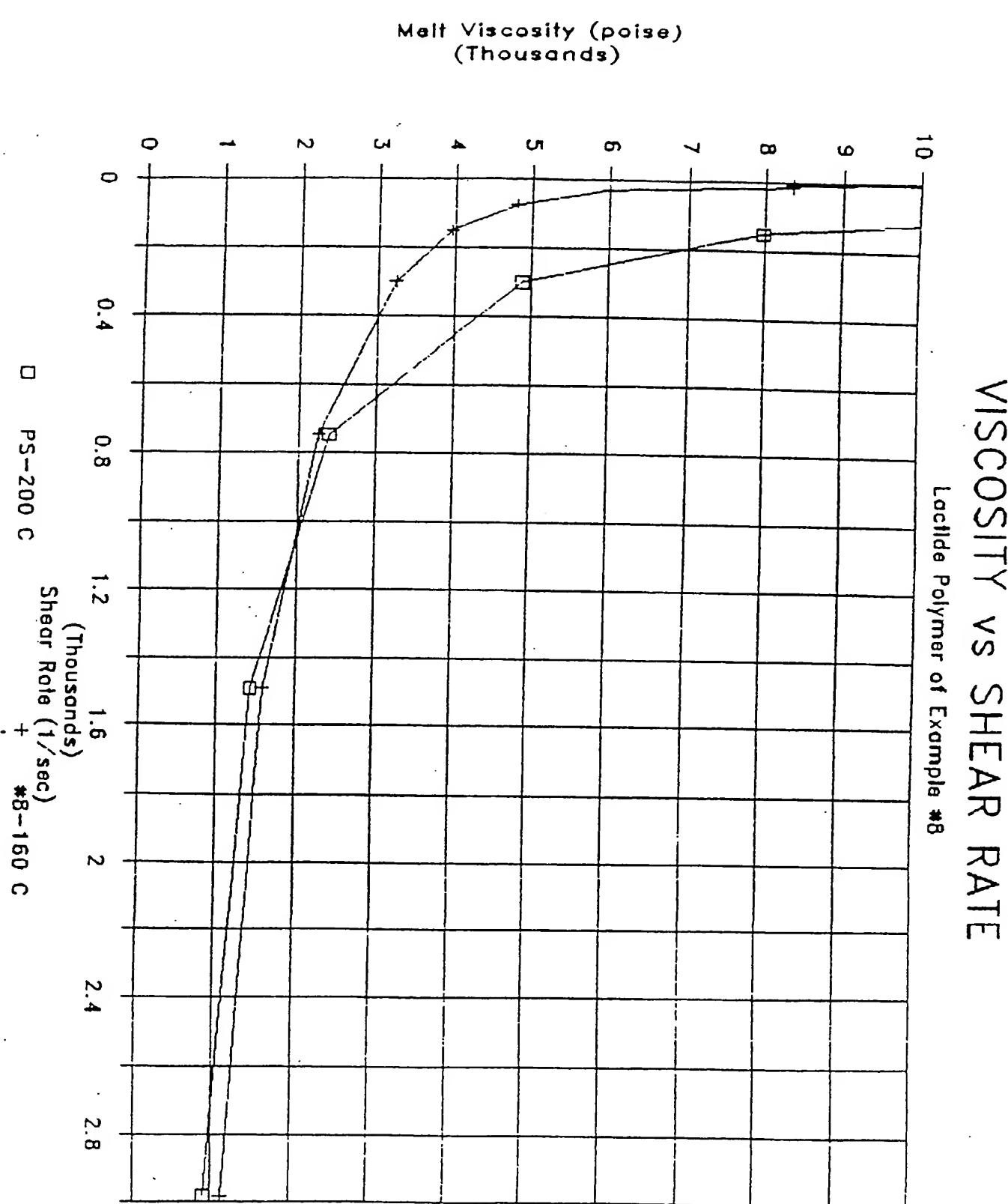
Figure 9.   MELT VISCOSITY COMPARISON OF POLYSTYRENE AND LACTIDE POLYMER OF EXAMPLE 8

□   PS-200 C   +   #8-160 C

(Thousands)
Shear Rate (1/sec)
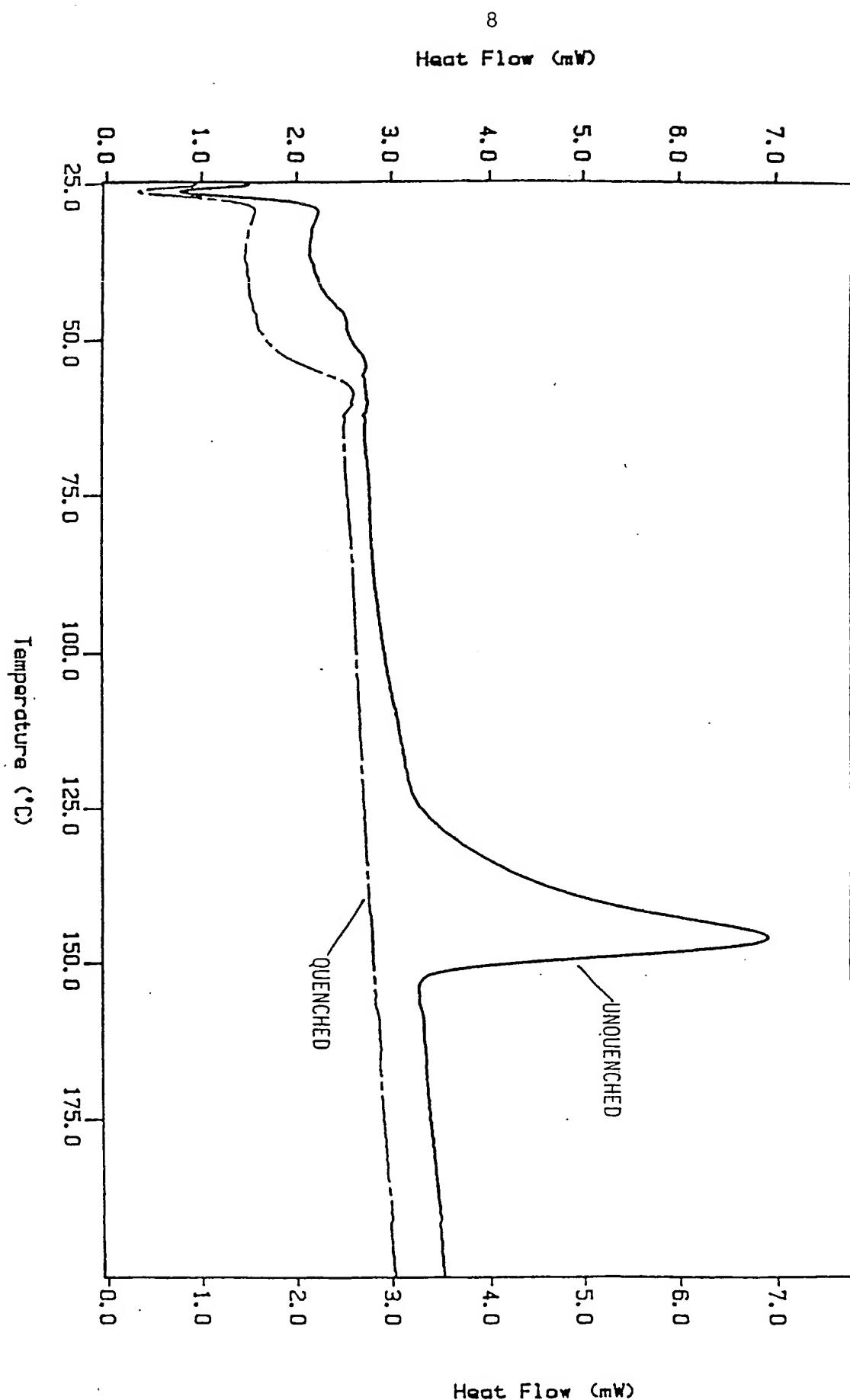
Figure 10. MATERIAL FROM EXAMPLE 8
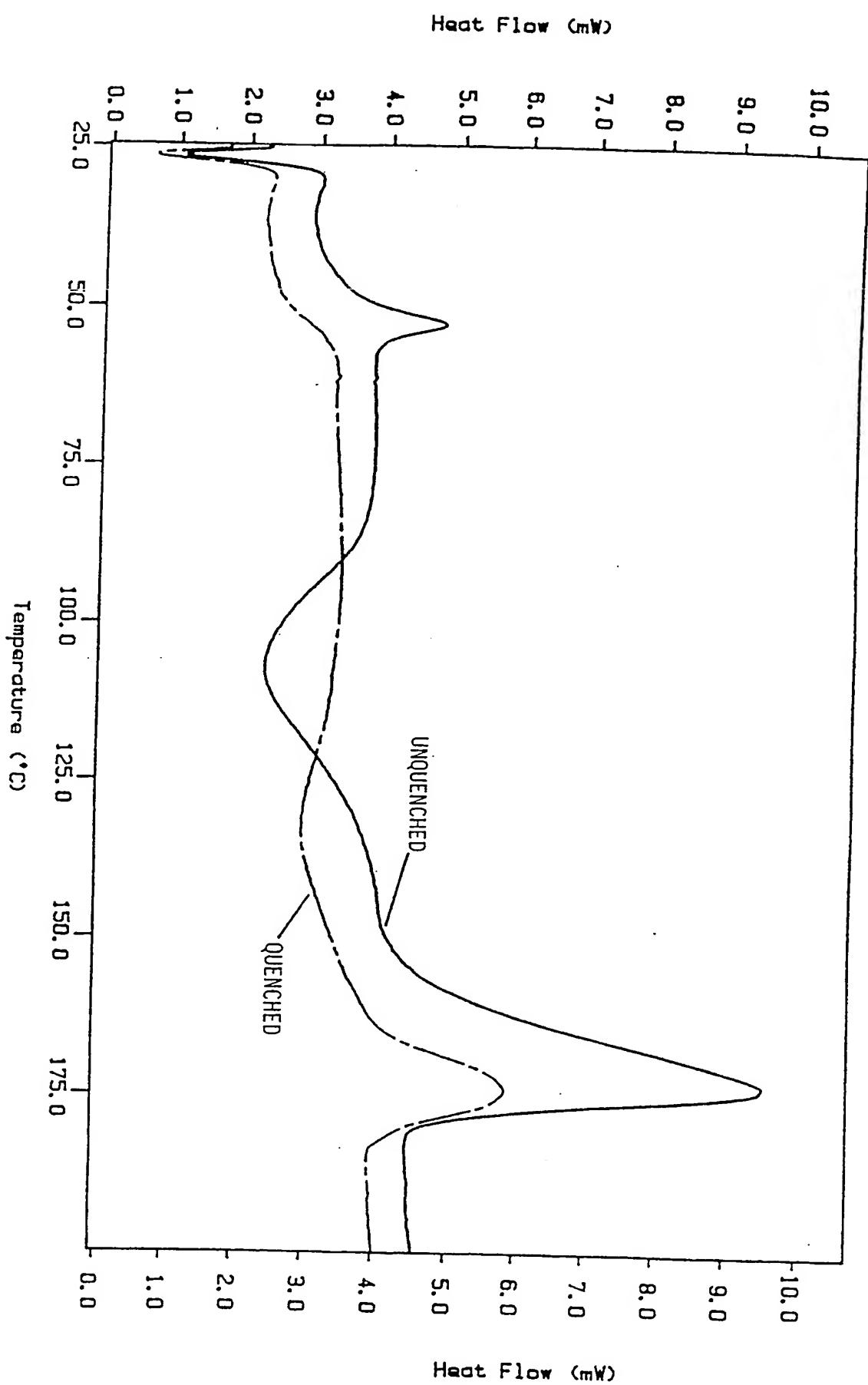
Figure 11. HOMOPOLYMER OF 100 PERCENT L-LACTIDE

Heat Flow (mW)
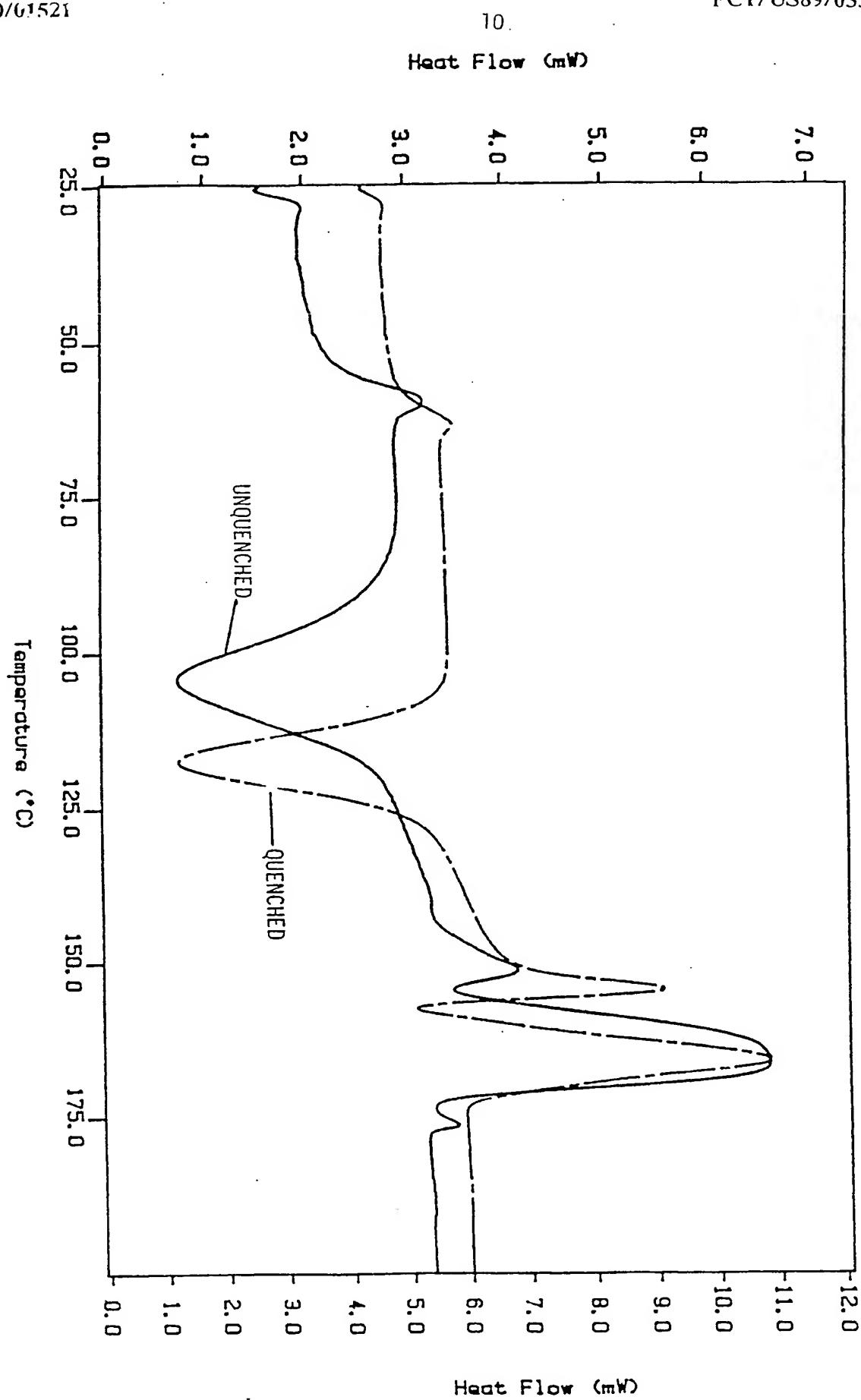
Figure 12.   BLEND OF COPOLYMER AND HOMOPOLYMER

Temperature (°C)

UNQUENCHED

QUENCHED

Heat Flow (mW)
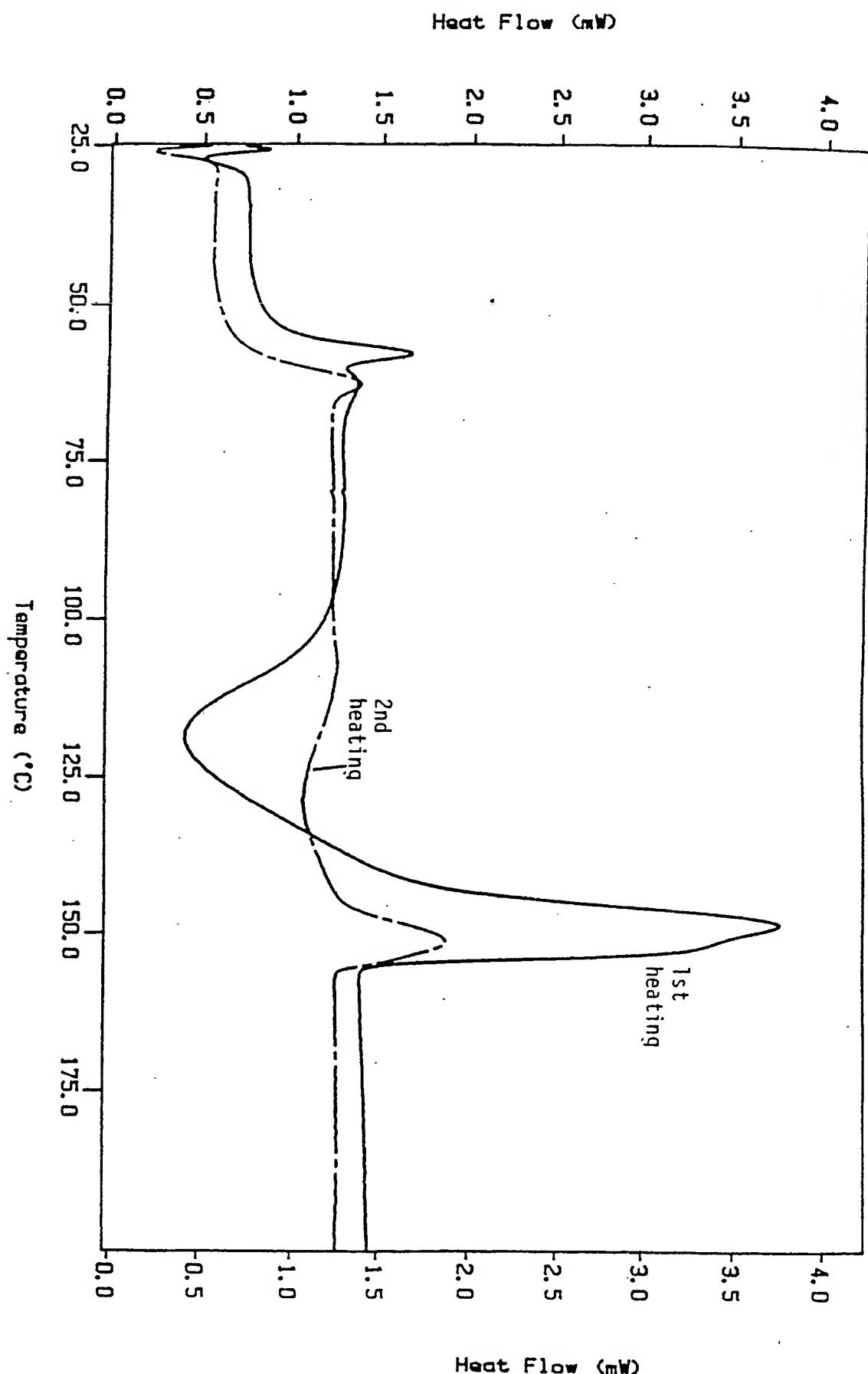
Figure 13. DSC OF 90/10, L-/D,L-LACTIDE COPOLYMER BLENDED
WITH 5 PERCENT POLYSTYRENE

INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 08 L 67/04, C 08 G 63/08

II. FIELDS SEARCHED

Minimum Documentation Searched *

Classification System	Classification Symbols
IPC5	C 08 L; C 08 G

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are included in the Fields Searched *

III. DOCUMENTS CONSIDERED TO BE RELEVANT *

Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
P,Y	Chemical Abstracts, volume 110, no. 24, 12 June 1989, (Columbus, Ohio, US), Bodmeier R. et al : "The effect of the addition of low-molecular weightpoly(DL-lactide) on drug release from biodegradable poly(DL-lactide) drug delivery systems. ", see page 409, abstract 219007f, & Int.J.Pharm. 1989, 51(1), 1- 8	1-4,7
Y	Chemical Abstracts, volume 108, no. 18, 2 May 1988, (Columbus, Ohio, US), Nakamura T. et al : "Surgical application of biodegradable films prepared from lactide--caprolactone copolymers. ", see page 391, abstract 156432b, & Adv. Biomater 1987, 7(), 759- 64	1-4,7

* Special categories of cited documents: ¹⁰

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
6th December 1989	1 2 JAN 1990

International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	T.K. WILLIS

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT   (CONTINUED FROM THE SECOND SHEET)

Category*	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	Chemical Abstracts, volume 105, no. 19, 10 November 1986, (Columbus, Ohio, US), Chawla Attar S et al : "In-vivo degradation of poly(lactic acid) of different molecular weights. ", see page 371, abstract 158776d, & Biomater.,Med.Devices,Artif.Organs 1986, 13(3), 153- 62	1-46
	--	
A	US, A, 4677191 (TANAKA ET AL) 30 June 1987, see abstract	1-46
	--	
A	US, A, 4728721 (YAMAMOTO ET AL) 1 March 1988, see column 2, line 31 - line 40; column 5, line 2 - line 6; abstract	1-46
	--	
A	US, A, 2703316 (ALLAN K. SCHNEIDER) 1 March 1955, see column 1, line 33 - line 45; column 2, line 10 - line 31; claims 1-7	1-46
	--	

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on   08/11/89
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4677191	30/06/87	EP-A-B- 0171907 EP-A-B- 0172636 JP-A- 61028521 US-A- 4683288 DE-A- 3567470 DE-A- 3567471	19/02/86 26/02/86 08/02/86 28/07/87 16/02/89 16/02/89
US-A- 4728721	01/03/88	EP-A- 0202065 JP-A- 62054760 US-A- 4849228	20/11/86 10/03/87 18/07/89
US-A- 2703316	01/03/55	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82